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# Course of sciences applied to military art

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DEPARTMENT OF APPLIED SCIENCES OF THE U. S. ARTILLERY SCHOOL.

COURSE OF

SCIENCES APPLIED TO MILITARY ART.

# CHEMICAL MANIPULATIONS.

— BY —

**JOHN P. WISSER,**

FIRST LIEUTENANT, FIRST ARTILLERY, INSTRUCTOR.

FORT MONROE, VIRGINIA.

PRINTED AT THE
UNITED STATES ARTILLERY SCHOOL.
1883.

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* * * * * * * * * * *

By order of
BREVET MAJOR GENERAL GETTY:

CONSTANTINE CHASE,
1st Lieutenant 3rd Artillery, A. D. C.,
Adjutant and Secretary of the Staff.

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# PREFACE.

This work is intended to serve as a Manual for use in the Laboratory: hence, the aim has been to make the various parts as complete as possible, to meet the special objects in view.

Part I contains a brief summary of the Principles of Chemistry and Chemical Analysis, necessary for a correct understanding of the processes in the practical work.

Part II contains the Special Analyses prescribed by the Programme of Instruction. The methods selected are, as far as possible, those which combine accuracy with economy of time and simplicity.

The list of works consulted not only serves to acknowledge my obligations in general, but also furnishes a table of books of reference for those who desire to pursue the subject further. My acknowledgements are due especially to the kindly interest, encouragement and instruction of Professor Kendrick, and of his successor, Professor Tillman, during my tour of duty as Instructor in the Department of Chemistry, Mineralogy, and Geology, at the United States Military Academy.

JOHN P. WISSER,
First Lieutenant First Artillery,
Instructor.

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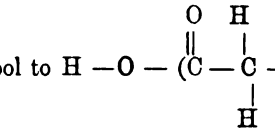
## CORRIGENDA.

| | | | |
|---|---|---|---|
| Page | 3, | line | 14, Change colon to semicolon. |
| " | 3, | " | 16, " " " |
| " | 14, | " | 28, read H — O — H for " H - OH. " |
| " | 15, | " | 10, change symbol to  |
| " | 15, | " | 20, read Three for " Those. " |
| " | 16, | " | 5, read $C_2$ $H_2$ $O_4$ for " $C_2$ $H_2$ O. " |
| " | 20, | " | 23, read Hyposulphurous for " Hydrosulphurous. " |
| " | 20, | " | 26, read Salts for **" Salts."** |
| " | 22, | " | 3, omit " by. " |
| " | 24, | " | 1, omit " for the mercuric oxide thus formed. " |
| " | 25, | " | 7, change colon to semi-colon. |
| " | 34, | " | 1, " " " |
| " | 34, | " | 15, read capillarity for " capilarity. " |
| " | 35, | " | 3, read Berzelius for " Berzeluis. " |
| " | 38, | " | 23, read liquids for " fluids. " |
| " | 54, | " | 24, read salt for " salts. " |
| " | 57, | " | 35, change colon to semi-colon. |
| " | 64, | " | 21, read wool for " wood. " |
| " | 65, | " | 32, read wire-gauze for " wire-gauge. " |
| " | 67, | " | 35, read quantitative for " qualitative. " |
| " | 67, | " | 37, " " " |
| " | 68, | " | 32, read ebullition for " ebulition. " |
| " | 98, | " | 3, read desiccator for " dessicator. " |
| " | 103, | " | 2, omit comma. |
| " | 106, | " | 23, omit comma. |
| " | 113, | " | 10, change comma to period. |
| " | 116, | " | 22, read emanations for " emenations. " |
| " | 126, | " | 12, insert to after " not. " |
| " | 134, | " | 8 from bottom, omit comma. |
| " | 136, | " | 2, read grammes for " gramme. " |

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# CHEMICAL MANIPULATIONS.

## PART I,

## GENERAL PRINCIPLES.

### SECTION 1.

#### Principles of Chemical Philosophy.

There are two classes of material phenomena: — First — those in which the substances involved preserve their identity, Second — those in which one or more of the substances involved are changed into new substances. The former are called *physical* phenomena, the latter, *chemical* phenomena. When a piece of copper is drawn out into wire, is rolled into sheets, is pulverized, is melted, is magnetized, or is made the medium of an electric current, the copper throughout preserves its identity and the phenomena are physical. When, on the contrary, the copper turns green by exposure to air and moisture, is heated to redness in the air, or is dissolved by nitric acid, it is converted into a new substance, malachite, cupric oxide or cupric nitrate, and the phenomena are chemical.

With about seventy exceptions, all substances may be decomposed, and are therefore *chemical compounds*, while the seventy which have not been resolved into simpler parts are called *elements*. There is some reason for believing that many, if not all, of these elementary substances may hereafter be decomposed. Of the seventy known elements, thirteen alone make up ninety-nine hundredths of the whole known mass of the earth: these are oxygen, silicon, aluminium, calcium, magnesium, potassium, sodium, iron, carbon, sulphur, hydrogen, chlorine and nitrogen.



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## ELEMENTS.

| | | | | | |
|---|---|---|---|---|---|
| Aluminium | Al | 27.0 | Mercury | Hg | 200.0 |
| Antimony | Sb | 120.0 | Molybdenum | Mo | 96.0 |
| Arsenic | As | 75.0 | Nickel | Ni | 58.8 |
| Barium | Ba | 137.0 | Nitrogen (6) | N | 14.0 |
| Bismuth | Bi | 210.0 | Norwegium (?) | Ng | 145.9 |
| Boron | B | 11.0 | Osmium | Os | 199.2 |
| Bromine | Br | 80.0 | Oxygen | O | 16.0 |
| Cadmium | Cd | 112.3 | Palladium | Pd | 106.2 |
| Caesium | Cs | 133.0 | Phosphorus | P | 31.0 |
| Calcium | Ca | 40.0 | Platinum | Pt | 194.8 |
| Carbon | C | 12.0 | Potassium | K | 39.1 |
| Cerium | Ce | 141.0 | Rhodium | Rh | 104.4 |
| Chlorine | Cl | 35.5 | Rubidium | Rb | 85.4 |
| Chromium | Cr | 52.2 | Ruthenium | Ru | 104.4 |
| Cobalt | Co | 58.8 | Scandium | Sc | 44.0 |
| Columbium (1) | Cb | 94.0 | Selenium | Se | 79.2 |
| Copper | Cu | 63.3 | Silicon | Si | 28.0 |
| Davyum (?) | Da | 154.0 | Silver | Ag | 108.0 |
| Decipium (?) | Dp | 159.0 | Sodium | Na | 23.0 |
| Didymium | D(2) | 140.0 | Strontium | Sr | 87.6 |
| Erbium | Er | 167.0 | Sulphur | S | 32.0 |
| Fluorine | F(3) | 19.0 | Tantalum | Ta | 182.0 |
| Gallium | Ga | 70.0 | Tellurium | Te | 128.0 |
| Glucinum (4) | Gl(5) | 13.9 | Terbium (?) | Tr | 171.0 |
| Gold | Au | 197.0 | Thallium | Tl | 204.0 |
| Holmium (?) | Ho | 162.0 | Thorium | Th | 231.4 |
| Hydrogen | H | 1.0 | Thulium (?) | Tm | 170.0 |
| Indium | In | 113.7 | Tin | Sn | 118.0 |
| Iodine | I | 126.8 | Titanium | Ti | 50.0 |
| Iridium | Ir | 192.7 | Tungsten | W | 184.0 |
| Iron | Fe | 56.0 | Uranium | U | 120.0 |
| Lanthanum | La | 139.0 | Vanadium | V | 51.3 |
| Lead | Pb | 206.9 | Ytterbium (?) | Yb | 173.0 |
| Lithium | Li | 7.0 | Yttrium | Y | 91.0 |
| Magnesium | Mg | 24.0 | Zinc | Zn | 65.2 |
| Manganese | Mn | 55.0 | Zirconium | Zr | 89.6 |

It has been observed from numberless analyses, that any given chemical compound always contains the same elements combined in the same proportions. This is the *Law of Definite Proportions*. Thus, water always consists of 11.111 parts, by weight, of Hydrogen and 88.889 of Oxygen.

Generally, the same elements unite in more than one proportion, forming two or more different compounds. When the two elements A and B are capable of uniting in

(1) Or Niobium, Nb.
(2) Or Di.
(3) Or Fl.
(4) Or Beryllium, Be.
(5) Or G.
(6) Or Azote, Az.

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several proportions, the several quantities of B which combine with a given quantity of A stand to one another in very simple ratios. This is the *Law of Multiple Proportions.* Thus, in the five oxides of nitrogen, the several quantities of oxygen which combine with 1.75 parts of nitrogen are 1, 2, 3, 4 and 5.

The observation of these two laws has led to the *Molecular Theory.*

**Molecules.** — The Molecular Theory assumes that matter is not continuous, but consists of molecules separated by a definite amount of space; the distance between the molecules being greatest in the gaseous state.

Molecules are the smallest masses into which a substance can be divided without destroying its identity; that is, they are the smallest particles of any substance which can exist by themselves.

The molecule is the unit of Physics, and the physical properties of a body depend on the relations of its molecules. These relations determine the three states of matter, solid, liquid and gas. In a solid, the molecules cohere firmly: in a liquid the molecules have great freedom of motion, but the motion is circumscribed within the liquid mass, and the liquid has a definite surface: in a gas the motion of the molecules is only circumscribed by the walls of the containing vessel, or by some extraneous force.

The *Kinetic Theory of Heat* assumes that the molecules of all bodies are in a constant state of motion, and this motion constitutes heat. *Temperature* is that effect of heat which is perceptible to the senses and can be measured by thermometers. Differences of temperature depend upon and indicate the relative energy of the molecular motion. The kinetic energy of each molecule, at the same temperature, is represented by $\frac{1}{2} m V^2$, in which $m$ is the mass and V the velocity at that temperature. When a body neither gains nor loses heat, the mean velocity of its molecules is constant; but, when the temperature is increased, this mean velocity must increase; hence, $\frac{1}{2} m V^2$ may represent the temperature of a body, and $\Sigma \frac{1}{2} m V^2$ its total heat. The mean velocity of the hydrogen molecules, at 0° C. and 30 in. Barometer, has been estimated as about 6097 feet per second.

The most general of the effects of heat is expansion; but, while each solid and liquid has its own rate and law of expansion, all gases have very nearly the same rate of expansion, and the amount is very nearly proportional to the increase of temperature. Gases expand $\frac{1}{273}$ of their volume at 0° C. for every degree of that scale; or, a confined mass of gas under constant volume gains or loses $\frac{1}{273}$ of its tension at 0° C. for a gain or loss of temperature of one degree. Hence, at — 273° C the tension would be nothing. Temperatures referred to — 273° C are called *absolute* temperatures, and are obtained by adding 273 to temperatures expressed on the centigrade scale.

*Problem.* — Given, ten cubic feet of marsh gas at a° C, required the volume at b° C.

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*Solution.* — Since gases increase in volume $\frac{1}{273}$ of their volume a 0° C. for every degree, 273 volumes at 0° would become at a°, 273 + $\frac{a}{273}$ of 273, or 273 + a volumes; and at b°, 273 + b volumes; and, as the ratio of the original to the new volumes, due to a given change of temperature, must be the same for all volumes, we have —

$$273 + a : 273 + b :: 10 : x, \text{ the volume at } b° \text{ C.}$$

Practically, we do not measure heat by determining the sum of the kinetic energies of all the molecules, but we use an arbitrary standard, called a *Unit of Heat*, which is the thermal force which corresponds to an interval of one degree in the temperature of the unit of weight of water taken at a standard temperature. The unit of weight here adopted is 1 kilogramme, and the standard temperature 0° C.

The amount of heat required to raise to the same extent, the temperature of equal weights of different substances, is by no means the same. This quantity of heat is capable of exact measurement and is called the *Specific Heat* of the substance. The specific heat of a body is the amount of heat, expressed in thermal units, which must be transferred, to or from the unit of weight of the body, taken at a standard temperature, in order to raise or lower its temperature one degree. Thus, the specific heat of lead is 0.0314; of iron, 0.1138; of air, 0.2377; of hydrogen, 3.4090.

In changes of state from solid to liquid, or from liquid to gas, heat is absorbed. In the inverse changes of state, heat is evolved. This is called *Latent Heat.* The latent heat of any particular substance, is the amount of heat, expressed in thermal units, which disappears in producing changes other than elevation of temperature in the unit of weight of that substance. Thus, the latent heat of lead is 5.4; of iron about 30; of water, 79; of steam, 537.

The production and consumption of heat, which accompany changes of state, or of volume, are explained by taking account of the *work* done. In the passage from solid to liquid, the molecules change their relative positions in opposition to the molecular forces. Hence, work is done, and, therefore, heat is absorbed: so, also, to a greater extent in evaporation. In the reverse changes of state, the molecules change their relative positions in accordance with the action of the molecular forces, and a certain velocity is imparted to them, which manifests itself in the form of heat. When a gas expands, heat becomes latent, because the pressure to which the gas is subjected is overcome. When a gas is compressed, heat is evolved, because the motion of the piston is communicated to the molecules and increases their velocity.

If these two theories which we have considered — the Molecular Theory and the Kinetic Theory of Heat, which are not chemical theories — be admitted, the following properties of matter can be proven mathematically, viz:

1st. The volume of a confined gas is inversely proportional to the pressure to which it is exposed.

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2nd. Equal volumes of all substances, when in the state of gas, and under like conditions of temperature and pressure, contain the same number of molecules.

3rd. The volume of a given mass of gas, under a constant pressure, varies directly as the absolute temperature.

These laws were discovered long before they were proven. The first is the *Law of Boyle* (called also the *Law of Mariotte*), discovered by Boyle in 1662; the second is the *Law of Avogadro*, discovered by an Italian of that name in 1814; the third is the *Law of Charles*, discovered in 1800.

From the Law of Avogadro the relative weights of equal volumes must be the same as the relative weights of molecules. Hence, the actual weights of equal volumes of different gases must be to each other as the actual weights of the molecules of these gases; or, the molecular weights of all substances are directly proportional to their specific gravities in the state of gas.

If hydrogen be adopted as the unit for specific gravities of gases, and the weight of its molecule as the unit of molecular weights, specific gravities and molecular weights would be represented by the same numbers. But it has been seen fit to adopt half the weight of the hydrogen molecule as the unit of molecular weights: hence, the molecular weight of any substance is twice its specific gravity in the state of gas. Therefore, to determine the molecular weight of any gas in terms of the half molecule of hydrogen, we have only to determine its specific gravity referred to hydrogen and multiply by two.

The molecular weights of substances are, therefore, the actual weights of their molecules in terms of the weight of a half molecule of hydrogen taken as unity. Calling this unit a *microcrith* (abbreviated m. c.), the hydrogen molecule weighs two microcriths, and the oxygen molecule, since its specific gravity is 16, weighs $16 \times 2 = 32$ m. c.

The size of a molecule of glass has been estimated as not less than $\frac{1}{500\,000\,000}$ of an inch; the number of molecules in one cubic inch of gas, at 0° C. and 30 in. Barometer, is abont $10^{23}$; a microcrith is about $33 \times 10^{-25}$ of a gramme.

**Atoms.** — According to the Atomic Theory the molecules of a substance are composed of *atoms*, and when, by chemical change, substances lose their identity and new substances are formed, the molecules are broken up into these smaller particles called atoms, and these re-arrange themselves in new groups to produce the new forms.

The atom is the smallest mass of an element that exists in any molecule. It is the unit of the chemist. As a rule, atoms cannot exist by themselves, every molecule consisting of at least two atoms, and this is true even of the elements. Thus, the molecule of oxygen gas consists of two atoms of oxygen; the molecule of nitric acid consists of one atom of nitrogen, three of oxygen, and one of hydrogen.

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From the Law of Definite Proportions we conclude that the atoms have definite weights. Chemical analysis determines the relative proportions of the different elements in a compound; and, if the number of atoms of each element in a molecule can be determined, evidently its atomic weight is obtained. Our conclusions as to the number of atoms of each element in a molecule rest principally on two classes of facts; the first is based on the determination of the smallest weight of an element which enters into the composition of a molecule, and the second on the specific heats of the elements.

The following is a list of some of the gaseous compounds of hydrogen. The molecular weights in microcriths are determined from the specific gravities, by multiplying by two. The last column gives the weight of hydrogen in each of the molecules, calculated from actual analysis.

| Compounds of Hydrogen. | Observed Sp. Gr. | Weight of Molecule. m. c. | Hydrogen by Analysis, in 1 part of compound. | Proportional part of H in molecule. | Weight of hydrogen in molecule m. c. |
|---|---|---|---|---|---|
| Hydrochloric acid | 18.32 | 36.5 | .0274 = | $\frac{1}{36.5}$ | 1 |
| Hydrocyanic acid | 13.67 | 27.0 | .0370 = | $\frac{1}{27}$ | 1 |
| Water | 9.00 | 18.0 | .1111 = | $\frac{2}{18}$ | 2 |
| Hydric sulphide | 17.19 | 34.0 | .0588 = | $\frac{2}{34}$ | 2 |
| Ammonia | 8.53 | 17.0 | .1765 = | $\frac{3}{17}$ | 3 |
| Marsh gas | 8.05 | 16.0 | .2500 = | $\frac{4}{16}$ | 4 |
| Alcohol | 23.28 | 46.0 | .1304 = | $\frac{6}{46}$ | 6 |
| Hydrogen | 1.00 | 2.0 | | | 2 |

The fourth column is derived from the third and second. For instance, in the case of hydrochloric acid, $\cdot\frac{0274}{1} = \frac{1}{36.5}$.

The last column shows that some substances contain one microcrith of hydrogen, others contain more than one; but no substance has been found containing a less weight of hydrogen than one microcrith. Hence, this is assumed as the mass of one of the atoms of hydrogen, and its weight is 1 m. c. It is adopted as the unit of atomic weights, because its weight is less than that of any other elementary atom.

In like manner, the smallest mass of oxygen entering any of its compounds is found to be 16 m. c., no smaller mass has yet been found to enter anywhere. Hence, this mass is assumed to be the atom of oxygen. It weighs 16 m. c.

The weights of the atoms of all the elements that furnish volatile compounds may be determined in the same way. It is evident that these atomic weights are the actual weights of definite masses of matter, — of atoms, each atom weighs so many microcriths.

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The second class of facts for determining the number of atoms in a molecule depends upon the observation, certainly approximately true, and probably absolutely, that the specific heat of all the atoms is the same. Hence, the same quantity of heat will raise the temperature of an atom of any of the elements one degree, or, will raise the temperature of a collection of equal numbers of atoms of any of the elements to the same extent.

The specific heats of the elements, or the heat required to raise equal weights to the same degree, have been accurately determined. The number of atoms in these equal weights must be inversely proportional to the atomic weights of the elements, or, the quotient of these equal weights by the atomic weights gives the number of atoms. If S, S′ represent the specific heats of two elements, m, m′ the weights of the corresponding atoms, w the equal weights compared, then —

$$S : S' :: \frac{W}{m} : \frac{W}{m'}, \text{ or } m\,S = m'\,S'.$$

Hence, *The product of the atomic weight of an element by its specific heat is a constant quantity.*

This is the *Law of Dulong* and *Petit*, discovered in 1819. The mean value of this product is found to be 6.34. To illustrate the use of this law, suppose it is found by analysis that silver chloride contains 35.5 parts of chlorine and 108 parts of silver. The atomic weight of chlorine is known to be 35.5, hence, this compound contains 1 atom of chlorine combined with 108 parts of silver, and it is required to determine the number of atoms of silver thus combined. If there is but one, it must weigh 108, if two it weighs 54 and so on. Now, the specific heat of silver is 0.057, and 6.34 divided by 0.057 is 111. Hence, allowing for inaccuracies, and remembering that it is only a question as to whether there are one or more atoms in the compound, 108 is evidently the weight of one atom.

There are several other methods for the determination of the atomic weights of elements, such as by equivalent substitution (*Chem. Fownes*, 12*th Ed. I, p.* 244); or, by considering the isomorphous relations of compounds (*Chem. Fownes*, 12*th Ed. I, p.* 249).

**Chemical Notation.** -- The initial letter of the Latin name of an element is used as the symbol of that element and represents one atom. When several names have the same initial, we add, for the sake of distinction, a second letter. Thus, O stands for one atom of oxygen, C for one atom of carbon, Ca for one atom of calcium, and so on. Several atoms of the same element are indicated by figures, which, to distinguish them from algebraic exponents, are placed to the right and a little below the letters. Thus $K_2$ stands for two atoms of potassium, $Cl_5$ for five atoms of chlorine. Sometimes, however, the separate symbols are written with dashes between them, thus O = O represents two atoms of oxygen.

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The molecule is expressed by grouping together the symbols of the atoms of which it is composed. Thus $KNO_3$ is the symbol for nitre, and represents one molecule. The weight of a molecule is the sum of the weights of its constituent atoms.

The multiplication of a group of dissimilar atoms is denoted by placing a numeral to the left of the group of symbols representing these atoms, or, by enclosing them in brackets and placing a numeral to the right and a little below the line. Thus three molecules of ammonium are represented by $3\ NH_4$, or by $(NH_4)_3$. The combination of two groups of atoms is represented by placing their symbols in juxtaposition with a dot between them. As this dot is equivalent to a + sign, a numeral placed to the left of the first group would not affect the second unless both be enclosed in parer thesis, and the numeral placed on the outside. Thus $3\ SO_3 . Fe_2 O_3 = 3\ SO_3 + Fe_2 O_3$, represents one molecule of normal ferric sulphate; but $3\ (SO_3 . Fe_2 O_3)$ represents three molecules of basic ferric sulphate, $SO_3\ Fe_2 O_3$.

**Reactions and Equations.** — Chemical changes are called *reactions* and the substances involved are called *reagents*. Reactions take place between molecules and consist in a breaking up of the molecules and a rearrangement of the atoms in new groups. Since matter is indestructible, the sum of the weights of the reagents must be equal to the sum of the weights of the products. Reactions are represented by equations, in which, the first member represents the reagents, the second the products. In every equation expressing a reaction, then, the sum of the number of atoms of each element in the first member must be equal to the sum of the number of atoms of the same element in the second member. Thus, the reaction between zinc and dilute hydrochloric acid, producing hydrogen gas and a solution of zinc chloride, is represented by the equation —

$$Zn + 2\ H\ Cl + Aq = Zn\ Cl_2 + Aq + 2\ H.$$

There are three principal kinds of reactions, *Analytical*, *Synthetical* and *Metathetical*.

Analytical reactions, are those in which a complex molecule is broken up into simpler ones. This usually takes place under the action of heat. Thus, when potassium chlorate is heated we obtain oxygen and potassium chloride,

$$K\ Cl\ O_3 = K\ Cl + 3\ O.$$

It may, however, take place without heat. Thus, when glucose ferments, it decomposes into alcohol and carbon dioxide,

$$C_6 H_{12} O_6 = 2\ C_2 H_6 O + 2\ CO_2.$$

Synthetical reactions are those in which atoms or molecules unite to form a more complex group. Thus, the burning of carbon in air produces carbon dioxide,

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$$C + 2\,O = CO_2.$$

Vapor of sulphuric oxide passed over heated barium oxide forms barium sulphate,

$$Ba\,O + SO_3 = Ba\,SO_4.$$

In this class of reactions, the reacting substances are generally opposed to each other in chemical properties. Thus, Ba O is a basic oxide, $SO_3$ is an acid oxide.

Metathetical reactions, are those in which the atoms of one molecule change places (according to atomicity) with the similar atoms of another molecule, or of several molecules. The reaction consists in the transformation of a compound by means of an auxiliary element or compound. It may take place in two ways —

*First* — By simple substitution,

$$H_2S + Sn = Sn\,S + 2\,H.$$

In this class of reactions the chemical properties of the auxiliary substance are generally similar to those of the substance replaced. Thus, an acid radical is replaced by another acid radical, a basic radical is replaced by another basic radical.

*Second* — By double decomposition,

$$Na\,Cl + Ag\,NO_3 = Ag\,Cl + Na\,NO_3.$$

$$H_2SO_4 + Ba\,Cl_2 = Ba\,SO_4 + 2\,H\,Cl.$$

In this class of reactions, if the body required be a salt, one of the reacting substances must contain the elements of the acid radical, the other, those of the basic radical. Thus, to form silver chloride, we select sodium chloride, which contains the acid radical chlorine, and silver nitrate, which contains the basic radical silver. A difference of solubility or volatility between the reacting compounds is generally essential. Thus, in the reactions above, silver chloride and barium sulphate are insoluble, while the other salts are soluble.

**Law of Volumes.** — The molecules of all elements which exist in the state of gas, with four exceptions, contain two atoms. Hence, their atomic weights are half their molecular weights ; but, since their molecular weights are double their specific gravities, their atomic weights and specific gravities are represented by the same numbers. Now, specific gravities are determined from the relative weights of equal volumes. Hence, equal volumes of the elementary gases, contain weights proportional to the atomic weights, and, therefore, the volumes of each of the elementary gases which make up a compound gas, are the same as the number of atoms of each element which enter the compound molecule. Thus,

To form H Cl will require 1 vol. H and 1 vol. Cl.
To form $H_2O$ will require 2 vol. H and 1 vol. O.
To form $H_3N$ will require 3 vol. H and 1 vol. N.



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If the smallest volume of an elementary gas which enters into any combination be called its combining volume, it may be stated that *the combining volumes of all elementary gases are equal.* This is the *Law of Equal Volumes*, discovered by Gay Lussac, in 1805.

From Avogadro's law, it follows, that the volumes of all single molecules are the same: but, the volume occupied by the molecule of hydrogen is twice the volume of the hydrogen atom. Hence, the molecules of all gases, simple or compound, must occupy twice the volume of the hydrogen atom.

Since specific gravities are determined by the weights of equal volumes, and since the molecular volumes of all gases are double the volume of the hydrogen atom (the standard of specific gravity), it follows that the specific gravity of any gas, simple or compound, is half its molecular weight; or, the molecular weight of any gas is double its specific gravity.

In support of this, Gay Lussac found, that no matter how many volumes of elementary or compound gases entered a compound, they were always condensed to two volumes. Thus —

2 vol. hydrogen + 1 vol. oxygen give 2 vol. water.
2 vol. nitrogen + 1 vol. oxygen give 2 vol. nitrogen monoxide.
1 vol. chlorine + 1 vol. hydrochloric acid gas.
1 vol. nitrogen + 3 vol. hydrogen give 2 vol. ammonia.
2 vol. ethylene + 2 vol. chlorine give 2 vol. ethylene chloride.

The four exceptions to the Law of Equal Volumes are mercury and cadmium, phosphorous and arsenic. The molecule of each of the two former contains but one atom, the molecule of each of the two latter contains four atoms, probably united thus . These exceptions are supposed to arise from anomalous conditions. Could these elements be examined at the temperatures at which they are perfect gases, they probably would not be exceptions.

**Stochiometry.** — Stochiometry is the application of the Law of Definite Proportions to chemical calculations. The chemical symbols enable us to calculate the amounts of the substances required in any process, as well as the amounts of the products it will yield. Two kinds of problems may arise — those involving weights and those involving volumes.

1. *Problems Involving Weights.* — In every reaction, the several terms stand for definite weights of the substances which they represent. The relative weights thus represented must be proportional to the total molecular weights of the substances which enter it, since these terms stand primarily for the weights of molecules. If a molecule is multiplied in the reaction, of course its molecular weight must be multiplied by the same number to obtain the total molecular weight.

Having the symbol of a substance given, its percentage composition may be cal-

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culated. As the weight of the molecule is to the total weight of each element in the molecule, so is one hundred parts to the percentage required. Thus, to determine the percentage composition of nitre, $KNO_3$, we have the proportions —

$$101.1 : 39.1 :: 100 : x = 38.67 \text{ per cent. potassium.}$$
$$101.1 : 14.0 :: 100 : y = 13.85 \text{ per cent. nitrogen.}$$
$$101.1 : 48.0 :: 100 : z = 47.48 \text{ per cent. oxygen.}$$
$$\overline{100.00}$$

Having a definite weight of a compound given, the weight of any of its constituents may be calculated in a manner similar to the preceding, substituting for one hundred in the proportions, the given weight of the compound. Thus, to determine the amount of iron in five grammes of the pure red oxide, $Fe_2O_3$, we have the proportion

$$160 : 112 :: 5 : x = 3.5 \text{ grammes iron.}$$

Having an equation expressing a reaction given, the weights of the reagents and products may be calculated. As the total molecular weight of the substance given is to the total molecular weight of the substance required, so is the actual weight of the substance given to the weight of the substance required. Thus, to determine the amount of hydric sulphide required to precipitate all the lead from a hot solution containing 30 grammes of lead chloride, and the weight of lead sulphide precipitated, we write the equation expressing the reaction

$$Pb\,Cl_2 + H_2\,S = Pb\,S + 2\,H\,Cl.$$

From which we obtain the proportions

$$278 : 34 :: 30 : x = 4 \text{ grammes hydrogen sulphide.}$$

$$278 : 239 :: 30 : y = 26 \text{ grammes lead sulphide.}$$

2. *Problems Involving Volumes.* — From Avogadro's Law, the volumes of all single molecules are the same. Hence, the total molecular volume represented by any symbol is equal to the number of molecules. Therefore, every equation expressing a reaction, represents the relative volumes of its reagents and products when in the state of gas.

Having the volume of one of the reagents or products in a reaction given, we can determine the volume of any one of the others by simple inspection of the equation expressing the reaction. Thus, to determine the number of litres of oxygen required to burn 10 litres of carbon monoxide, and the number of litres of carbon dioxide produced, we write the equation expressing the reaction

$$2\,CO + 2\,O = 2\,CO_2.$$

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Remembering that 2 O is but one molecule of oxygen, evidently, 2 volumes of CO require 1 volume of O and produce 2 volumes of $CO_2$. Hence, 10 litres of CO will require 5 litres of O, and 10 litres of $CO_2$ will be produced. The volumes found, are, of course, those measured at the same temperature as that at which the volume of CO is given.

Having the weight of one of the reagents or products in a reaction given, we can calculate the volume of any gas involved; or, having the volume of any gas in a reaction given, we can calculate the weight of any of the reagents or products.

As one half the molecular weight of the substance, whose weight is given or sought, is to the number of molecules of the substance whose volume is given or sought, so is the weight in criths[1] of the first, to the volume in litres of the second. Thus, to determine the number of grammes of chalk required to yield one litre of carbon dioxide, we have the equation expressing the reaction —

$$\underset{100}{Ca\,CO_3} + 2\,H\,Cl = Ca\,Cl_2 + H_2\,O + CO_2.$$

½ 100 : 1 :: x : 1, hence, x = 50 criths = 50 × 0.0896 grm. = 4.48 grms. chalk.

**The Old and the New Chemistry.** — The difference between the old and the new chemistry can now be made apparent. Avogadro's law is the basis of modern chemistry as much as the law of gravity is the basis of astronomy. It depends only on the molecular theory. It is proven by all known chemical phenomena, and is continually leading to new discoveries. It has led to a correct understanding of the structure of molecules, and has thus become one of the most valuable aids to discovery which science has received. It has been particularly fruitful in the domain of organic chemistry. The latest, and most important of the discoveries resulting from it, are the great coloring matters, the aniline dyes and alizarin, products of coal tar, manufactured so cheaply and on such an enormous scale, as to have entirely driven from the market many of the old dyes. The aniline dyes, which, up to the year 1858 were scarcely known, now furnish every color and all tints and shades of color, so that England, (as Hofmann predicted in 1862), instead of disbursing her annual millions for these substances, now sends her blues to indigo-growing India, her crimson to cochineal-producing Mexico, and her substitutes for quercitron, saffron, and madder, to the countries which heretofore exported these coloring matters to the world. These were the result of purely theoretic study, and would have been impossible under the old chemistry.

The difference in the two systems may be illustrated by the simple case of water. The old symbol OH represented the percentage composition as well as the new; for, O represented 8 parts of oxygen and H represented 1 part of hydrogen, by weight.

(1) The weight of 1 litre of hydrogen at the standard temperature and pressure. It is equal to 0.0896 gramme.

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There was no particular reason for writing it OH, and, of course, there was no reason why O should be 8. The symbol was adopted on account of its simplicity, and the value of O resulted, when H was taken as unity. It represented the percentage composition, and it represented no more. It told all that was then known, but the new symbol $H_2O$ tells us much more. It represents the composition, 8 parts by weight, of oxygen, to 1 part of hydrogen, no better than the old, but it also tells us that the molecule of water is composed of one atom of oxygen and two atoms of hydrogen, that two volumes of hydrogen combine with one volume of oxygen to form water, and that out of these two volumes of hydrogen and one volume of oxygen two volumes of water-vapor are produced.

**Chemical Equivalency.** — If, in a solution of silver nitrate, metallic mercury be placed, the silver will be precipitated and part of the mercury dissolved. If the solution of mercuric nitrate be decanted, and a strip of copper placed in it, the mercury will be displaced by the copper. In like manner, the copper may be displaced by zinc, and the zinc by magnesium. By proper analytical methods, the relative quantities, by weight, of the elements which thus replace one another can be determined, and it is found, that when one element replaces another in combination, the replacement always takes place in fixed or definite proportions. Thus, in the replacements above mentioned, the following are the weights of the replacing elements, supposing that 108 milligrammes of silver were precipitated from the first solution: 100 milligrammes mercury, 31.7 copper, 32.6 zinc, 12 magnesium.

The relative weights of the elements which thus replace one another are called the *equivalent weights*. In some cases, one atom of one element is equivalent to one atom of another element. In other cases it may be the equivalent of two, three, or more atoms. Thus, when silver nitrate is precipitated by hydrochloric acid, one atom of silver replaces one atom of hydrogen; when calcium carbonate is decomposed by hydrochloric acid, one atom of calcium replaces two atoms of hydrogen; when antimony is dissolved in hot hydrochloric acid, one atom of antimony replaces three atoms of hydrogen.

$$Ag\,NO_3 + H\,Cl = Ag\,Cl + H\,NO_3.$$

$$Ca\,CO_3 + 2\,H\,Cl = Ca\,Cl_2 + H_2O + CO_2.$$

$$Al + 3\,H\,Cl = Al\,Cl_3 + 3\,H.$$

This relation of the elements is called their *quantivalence* (also called equivalency, or atomicity), and, regarding the hydrogen atom as the unit, elements are *univalent*, *bivalent*, *trivalent*, *quadrivalent*, *quinquivalent*, according as one of their atoms replaces one, two, three, four, five atoms of hydrogen. Quantivalence is indicated by means of dashes, the number of dashes corresponding to the quantivalence.



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The quantivalence of an element is also shown by its power of replacing other atoms whose quantivalence is known. Thus, mercury is bivalent because 200 m. c. (or one atom) replace 216 m. c. (or two atoms) of silver, and silver is known to be univalent.

The quantivalence of an element corresponds, also, to its combining, saturating or atom-fixing power. Thus, in the following compounds the atoms of univalent elements hold one atom of hydrogen, of bivalent two, of trivalent three, and of quadrivalent four.

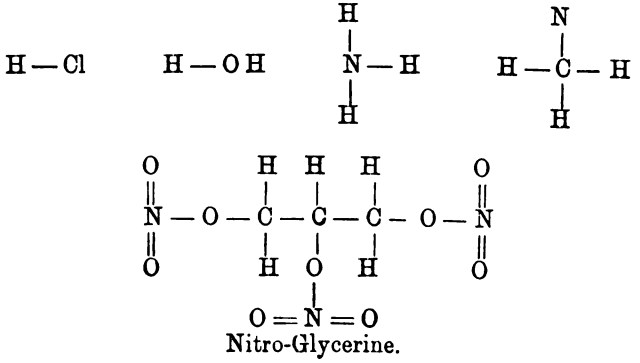
$$H-Cl' \qquad HH-O'' \qquad HHH-N''' \qquad HHHH-C^{IV}.$$

Univalent elements are called *monads*, as $Na'$.
Bivalent elements are called *dyads*, as $Ca''$.
Trivalent elements are called *triads*, as $Al'''$.
Quadrivalent elements are called *tetrads*, as $C^{IV}$.
Quinquivalent elements are called *pentads*, as $P^{V}$.
Sextivalent elements are called *hexads*, as $W^{VI}$.

Atoms of even degrees of equivalency are called *artiads*; those of uneven equivalency are called *perissads*.

The quantivalence of elements is by no means always the same. Thus, iron in the *ferrous* compounds is bivalent, but in the *ferric* compounds it is trivalent. Yet, the variations of quantivalence are usually limited, and are either all even or all odd. Thus, sulphur may be sextivalent, quadrivalent, and bivalent, but is never trivalent or univalent.

**Structural Symbols.** — The quantivalence of an atom is the measure of its atom-fixing power. Hence, in compounds like $H\,Cl'$, $H_2\,O''$, $H_3\,N'''$, $H_4\,C^{IV}$, the hydrogen atoms must be regarded as united with the dominant atom, or atom of highest quantivalence, and not with each other. This is represented by what are called *structural formulæ*,



Nitro-Glycerine.

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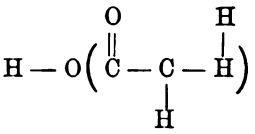
in which the quantivalence of each atom is indicated by the number of dashes connected with it.

These formulæ do not represent the relative positions of the atoms in space, but they do represent the manner in which we conceive the atoms in the molecule to be connected. These formulæ, representing the definite structure of molecules, are the result of chemical investigation. Thus, we can replace either one, two, or three, of the four atoms of hydrogen in acetic acid by chlorine gas, but we cannot replace the fourth, hence, we conclude, that it stands in a different relation to the molecule; and, this is evident in the formula deduced from this and other evidence,



The three replaceable atoms are connected directly with a carbon atom; whereas, the fourth, which is not thus replaceable, is connected indirectly through an atom of oxygen.

In the structural symbol for nitro-glycerine we have an explanation of its action. The ordinary symbol is $C_3 H_5 (NO_2)_3 O_3$; but this does not explain its explosive power: for, in its explosion, the carbon and hydrogen are simply oxidised and converted into gaseous products. But the oxygen required is only that of the molecule, hence, it is not apparent why the carbon and hydrogen are not already combined with oxygen in the molecule, and their affinities satisfied. An examination of the structural formula gives the explanation. Those of the oxygen atoms are partially combined with carbon and partially with nitrogen, the rest of the oxygen atoms are united with the nitrogen atoms, and not with those of either carbon or hydrogen.

When the substance explodes, the oxygen-atoms at one end of the molecule rush for the atoms of carbon and hydrogen at the other end; and, as this takes place in the molecule, the combustion is essentially instantaneous.

It is seen, then, that in ordinary compounds, every unit of equivalency in the atoms is satisfied by combination with a unit of some other atom. Therefore, the sum of the atomicities of all the atoms of a compound must be an even number. This is called the *Law of Even Numbers.*

**Radicals.** — If one of the atoms of a molecule, in which every unit of equivalence is satisfied by combination with some other unit, be removed, the remaining atom, or group of atoms, is called a *radical* — it will have a combining power equal to the units of equivalence removed. Thus, H Cl is a molecule in which the unit of equivalence of the chlorine atom, is satisfied by combination with the unit of equivalence of the hydrogen atom. If, now, the atom of hydrogen be removed, Cl, the chlorine atom remaining, is a *simple* radical, and its combining power is unity. Again,

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$CO_2 H_2$ is the molecule of formic acid. If one atom of hydrogen be removed, we obtain the *compound* radical $CO_2 H$ — the acid radical of the formates, whose combining power is unity. If the univalent radical HO be removed from $CO_2 H_2$ we obtain the univalent radical CO H. If the bivalent radical $(OH)_2$ be removed from the molecule of oxalic acid, $C_2 H_2 O$, we obtain the bivalent radical $C_2 O_2$, and so on.

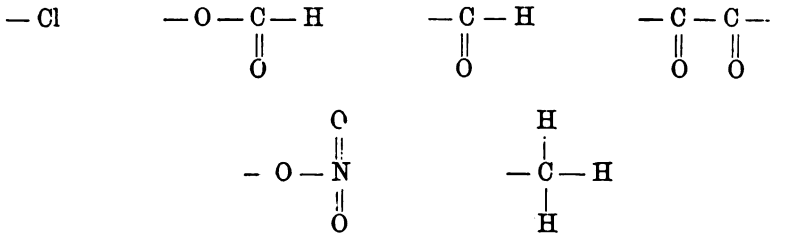
These groups of atoms seem to sustain the same relations to the compounds they leave or enter, as the elements themselves. Thus, in the nitrates we have the compound radical $NO_3$ bearing the same relation to the metals that the simple radical Cl bears in the chlorides.

$$K\,(Cl) \qquad K\,(NO_3)$$

$$Ca\,(Cl)_2 \qquad Ca\,(NO_3)_2$$

These radicals cannot, as a rule, exist in the free state, but aggregates of them may exist. Thus, the radical methyl, $CH_3$, does not exist as such, but dimethyl $C_2 H_6$, having the same percentage composition, is a known compound.

If radicals are formulated according to the structural system, some of the bonds will remain unclosed — the number of unclosed bonds indicating the atomicity of the radical. Thus, the compounds above referred to may be written,



**Theories of Molecular Structure.** — From the observed effects of electrolysis, causing certain elements to be evolved at the positive pole, and certain others at the negative pole, it was inferred that the atoms had an opposite polarity to that of the poles to which they were attracted, and it would follow that there must be a duality in all chemical compounds, the elements uniting by twos to form binary compounds, the binary uniting by twos to form ternary compounds, and so on, and this duality was supposed to be preserved in the complex molecule. Thus, alum is written $K_2 O . SO_3 . Al_2 . O_3 . 3\ SO_3$. This is the *Dualistic Theory* of the old chemistry. It undervalued essential circumstances and misinterpreted important facts. For instance, hydrogen was regarded as an accidental constituent of acids and alkalies, whereas, now, it is regarded as essential ; and, when an alkali was neutralized by an acid, the reaction was supposed to consist in the direct union of two oxides, whereas, it actually consists in the replacement of the hydrogen. Formulæ resembling the dualistic are still used, but only to represent the neutralization of the units of equiv-

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alency of the elements of a compound, or the manner in which a compound is formed of groups of atoms, or splits up into groups under the action of reagents.

Avogadro's law and the subject of quantivalence have led to the new theory of molecular structure. According to this, when atoms or molecules unite, a general chemico-molecular disintegration obtains, resulting in the formation of a single molecular group. A molecule is, therefore, a complex unit, all of whose parts are bound together by atomic bonds. Thus, alum is written $K\ Al\ S_2\ O_8$. This is the *Unitary Theory*, now generally accepted.

**Nomenclature.** — The names of the elements are not conformed to any fixed rules. Those known before 1787 retain their old names. Newly discovered elements are generally named from some marked property. The names of the recently discovered metals have the common termination *ium*.

Compounds consisting of two elements are called *binary* compounds.; of three, *ternary* compounds; of four, *quaternary* compounds; of five, *quinary* compounds, and so on.

*Bases* are hydrates — compounds formed from water by replacing half of its hydrogen with some metal or compound radical acting like a metal.

$$H_2\ O + Na = Na\ HO + H.$$

$$2\ H_2\ O + Ca = Ca\ H_2\ O_2 + 2\ H.$$

*Basic oxides* are metallic oxides — compounds of the metals with oxygen, and may be regarded as formed by replacing all the atoms of hydrogen in one or more molecules of water with the atoms of some metal.

*Acids* are compounds containing hydrogen, which is replaceable by metallic elements or basic radicals, and is united, in the molecule, to a non-metallic atom, or negative radical, called an *acid radical*. Those in which the two parts of the molecule are united by oxygen atoms are called *oxygen acids*, as $H - O - NO_2$, $H_2 = O_2 = SO_2$. Those in which the hydrogen atoms are united directly to the radical, without any such connection, are called *hydracids*, as $H - Cl$, $H_2 = S$, $H - CN$. The *basicity* of an acid is determined by the number of hydrogen atoms it contains replaceable by basic radicals. Acids are *monobasic*, *bibasic*, *tribasic*, etc., according as they contain one, two, three, etc., atoms of replaceable hydrogen. Thus, $H\ Cl$, $H\ NO_3$ are monobasic, $H_2\ S$, $H_2\ SO_4$, $H_2\ CO_3$ are bibasic, $H_3\ PO_4$ is tribasic.

*Acid oxides* are compounds bearing the same relation to acids which metallic oxides bear to hydrates or bases, and may be regarded as formed from one or more molecules of water, by replacing all the hydrogen by negative or acid radicals.

$$H_2\ O + SO_2 = SO_3 + H_2.$$

$$H_2\ O + (NO_2)_2 = N_2\ O_5 + H_2.$$

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Many acid oxides unite with water to form acids.

$$SO_3 + H_2O = H_2SO_4.$$

*Salts* are compounds formed by replacing one or more of the replaceable hydrogen atoms in any acid, with metallic atoms, or basic radicals,

$$H_2SO_4 + Zn = ZnSO_4 + H_2,$$

or, by replacing one or more of the replaceable hydrogen atoms in any base, with non-metallic atoms, or acid radicals,

$$ZnO_2H_2 + SO_2 = ZnSO_4 + H_2.$$

Salts are also formed by the direct union of acid and basic oxides, and by the double decomposition of compounds.

A *normal salt*, is one formed by replacing all the replaceable hydrogen atoms of an acid by basic radicals, or all the replaceable hydrogen atoms of a base by acid radicals.

$$H_2CO_3 + K_2 = K_2CO_3 + H_2.$$

$$2KHO + CO_2 = K_2CO_3 + H_2O.$$

A *basic salt*, is one formed by replacing only part of the replaceable hydrogen atoms of a base by acid radicals.

$$\underset{\text{acetic acid}}{PbO_2H_2 + C_2H_4O_2} = \underset{\text{basic lead acetate}}{PbO_2(C_2H_3O)H} + H_2O.$$

Another kind of basic salt, is one in which the number of molecules of acid oxide is less than the number of oxygen atoms in the basic oxide. Tribasic lead nitrate may be written $3\,PbO.N_2O_5$, in which there is one molecule of acid oxide, $N_2O_5$, to three atoms of oxygen in the basic oxide $3\,PbO$.

An *acid salt*, is one formed by replacing only part of the replaceable hydrogen atoms of an acid by basic radicals.

$$H_2SO_4 + K = \underset{\text{acid potassium sulphate}}{HKSO_4} + H.$$

Another kind of acid salt (called also an anhydro-salt) is one in which the number of molecules of acid oxide is greater than the number of oxygen atoms in the basic oxide. Sodium bi-sulphate may be written $Na_2O.2\,SO_3$, in which there are two molecules of acid oxide $2\,SO_3$ to one atom of oxygen in the basic oxide $Na_2O$.

Binary compounds are named by placing after the name of one of the elements, that of the other with the termination *ide*. In the case of compounds of oxygen, the

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name of the element in combination with the oxygen is usually placed first, and, in case of metallic or hydrogen compounds, the name of the metal, or hydrogen, is usually placed first. Compounds of oxygen are called oxides, of chlorine chlorides, of sulphur sulphides, etc.

| | Old Names. |
|---|---|
| $K_2O$ is Potassium Oxide. | Potash. |
| Ca O is Calcium Oxide. | Lime. |
| $Ba Cl_2$ is Barium Chloride. | Chloride of Barium. |
| $H_2S$ is Hydrogen Sulphide. | Sulphuretted Hydrogen. |

When two elements combine in but two proportions, the compounds are distinguished by the terminations *ous* and *ic*, the former for the lower degree of oxidation, chlorination and so forth, the latter for the higher degree.

| | Old Names. |
|---|---|
| Fe O is Ferrous Oxide. | Protoxide of Iron. |
| $Fe_2O_3$ is Ferric Oxide. | Sesquioxide of Iron. |
| $N_2O$ is Nitrous Oxide. | Protoxide of Nitrogen. |
| NO is Nitric Oxide. | Deutoxide of Nitrogen. |
| $SO_2$ is Sulphurous Oxide. | Sulphurous Acid. |
| $SO_3$ is Sulphuric Oxide. | Sulphuric Acid. |
| $Sn Cl_2$ is Stannous Chloride. | Protochloride of Tin. |
| $Sn Cl_4$ is Stannic Chloride. | Perchloride of Tin. |

The names of the oxides of the alkaline, alkaline earth, and earth metals are commonly written by adding the termination *a* to the name of the metal.

$Na_2O$ is Sodium Oxide, or Soda.
Mg O is Magnesium Oxide, or Magnesia.
Ba O is Barium Oxide, or Baryta.
$Al_2O_3$ is Aluminium Oxide, or Alumina.

The hydracids retain the names of the old nomenclature as acids.

| | Old Names. |
|---|---|
| H Cl is Hydrogen Chloride, or | Hydrochloric Acid. |
| H C N is Hydrogen Cyanide, or | Hydrocyanic Acid. |
| $H_2S$ is Hydrogen Sulphide, or | Hydrosulphuric Acid. |

When two elements combine in more than two proportions, the several degrees of oxidation, chlorination, etc., are indicated by the prefixes *mono*, *di*, *tri*, *tetra*, *penta*, etc. A compound intermediate between a *mono* and a *di* compound is called a *sesqui* compound.

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Cr O is Chromium Monoxide.
$Cr_2 O_3$ is Chromium Sesquioxide.
$Cr O_2$ is Chromium Dioxide.
$Cr O_3$ is Chromium Trioxide.
$K_2 S$ is Potassium Monosulphide.
$K_2 S_2$ is Potassium Disulphide.
$K_2 S_5$ is Potassium Pentasulphide.

Bases are named by adding to the name of the metal (with the terminations *ous* and *ic*, if necessary) the word *hydrate*.

K H O is Potassium Hydrate.
$Ba H_2 O_2$ is Barium Hydrate.
$Fe O_2 H_2$ is Ferrous Hydrate.
$Fe_2 O_6 H_6$ is Ferric Hydrate.

Acids are named from the most characteristic element of the acid radical, modified by prefixes and terminations as before The specific names of the organic acids are generally arbitrary. The oxygen acids whose names end in *ous* and *ic*, have, usually, the composition of the corresponding oxides with the elements of water. The prefixes *hyper* (or *per*) and *hypo* are sometimes used. The former indicates more, the latter, less of the electro-negative element than exists in the compound to which the name is prefixed.

H F is Hydro-Fluoric Acid.
$HNO_3$ is Nitric Acid.
$H_2 SO_4 = H_2 O . SO_3$ is Sulphuric Acid.
$H_2 SO_3 = H_2 O . SO_2$ is Sulphurous Acid.
$H_2 SO_2$ is Hydrosulphurous Acid.
$H Cl O_3$ is Chloric Acid.
$H Cl O_4$ is Perchloric Acid.

**Salts.** — The name of a salt is formed from the name of the acid from which the salt is derived, preceded by the names of the basic radicals. Salts derived from acids ending in *ous* have the termination *ite*: those derived from acids ending in *ic* have the termination *ate*. The basic radicals may also have prefixes and suffixes as before.

$Ca CO_3$ is Calcium Carbonate.
$Ba SO_3$ is Barium Sulphite.
$Fe SO_4$ is Ferrous Sulphate.
$Fe_2 (SO_4)_3$ is Ferric Sulphate.

The tendency among scientific men to-day, is to give such a name to a compound as will express its composition quantitatively as well as qualitatively; that is, to indicate the elements that enter it, as well as the proportions in which they enter.

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$Fe_2S$ is Diferrous Sulphide  $FeS_2$ is Ferric Disulphide.
$N_2O_3$ is Dinitric Trioxide.  $Fe_3O_4$ is Triferro Tetroxide.
$Na_2O_7B_4$ is Disodic Tetraborate.
$H(NH_4)Na(PO_4)$ is Hydro-Ammonio-Sodic Phosphate.

**Determination of Molecular Weights.** — To determine the molecular weight of a compound, the percentage composition is first determined by analysis. From this is constructed what is called the *empirical formula*, which gives the simplest possible expression of the composition of the substance. Thus, the composition of acetic acid by analysis is

| | |
|---|---|
| Carbon | 40.00 |
| Hydrogen | 6.67 |
| Oxygen | 53.33 |
| | 100.00 |

The relative number of atoms of each of these elements in the compound, is determined by dividing these quantities by their respective atomic weights,

$$\frac{40.00}{12} = 3.33. \qquad \frac{6.67}{1} = 6.67. \qquad \frac{53.33}{16} = 3.33.$$

But, 3.33 : 6.67 : 3.33 :: 1 : 2 : 1,

Hence, $CH_2O$ is the empirical formula.

The molecular formula expresses the absolute number of atoms of each element in the molecule. It may be the same as the empirical formula, or it may be some multiple of it. To determine the molecular formula from the empirical, several considerations are taken into account.

First, the number of atoms of hydrogen it contains replaceable by acid or basic radicals. The empirical formula of nitric acid is $HNO_3$, to determine its molecular formula, we study its salts and find it is monobasic ; for there is but one potassium, sodium, ammonium, or silver nitrate. If it were polybasic there would be several. We analyze silver nitrate and find that 100 parts of the salt contain 63.53 parts of silver. We know that the atomic weight of silver is 108, therefore 108 must be to the molecular weight of silver nitrate as 63.53 is to 100.

63.53 : 100 :: 108 : x = 170, the molecular weight of silver nitrate.

But silver nitrate differs from nitric acid only in having an atom of hydrogen in place of an atom of silver : hence. the molecular weight of nitric acid must be 170 — 108 + 1 = 63.

Again, we found the empirical formula of acetic acid to be $CH_2O$ ; but, by studying its salts, we find that only *one-fourth* of the hydrogen it contains is replaceable by metals, therefore, its formula must be $C_2H_4O_2$ or some multiple of this.



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From the molecular weight of any acid we can easily deduce the molecular weight of all its salts.

Secondly, by the Law of Even Numbers must be satisfied. Thus, the empirical formula of cyanogen is $C^{IV}\ N'''$; but in this, the sum of the atomicities is an odd number, seven, hence its molecular formula must be some even multiple of this, as $C_2 N_2$ or $C_4 N_4$, etc.

Thirdly, Its specific gravity when in a state of gas must be half its molecular weight. Thus, the specific gravity of acetic acid gas is nearly 30, referred to hydrogen; hence, its molecular weight must be 60. Its molecular formula is, therefore, $C_2 H_4 O_2$. The specific gravity of cyanogen gas is 26, its molecular weight is, therefore, 52, and its molecular formula must be $C_2 N_2$. The empirical formula of benzene is C H, its specific gravity in the state of gas is about 39; hence, its molecular weight is 78, and its molecular formula must be $C_6 H_6$.

When these methods are inapplicable, we attempt to find the symbol which expresses the composition in the simplest terms. Thus, the analysis of cane-sugar gives

| | |
|---|---|
| Carbon | 42.06. |
| Hydrogen | 6.50. |
| Oxygen | 51.44. |

The relative number of atoms will be,

$$\frac{42.06}{12} = 3.50 \text{ carbon}, \quad \frac{6.50}{1} = 6.50 \text{ hydrogen}, \quad \frac{51.44}{16} = 3.22 \text{ oxygen};$$

but fractional atoms cannot exist, hence, the true numbers must be some multiple of these. The hydrogen and oxygen are evidently nearly in the proportion to form water, and the carbon and hydrogen are nearly in the proportion 12 : 22; therefore, we conclude the symbol is $C_{12} H_{22} O_{11}$. For all we know it may be any multiple of this, but none of its reactions has contradicted the assumption that this is its formula and so it has been adopted.

**Isomerism.** — Several compounds are said to be isomeric when they have the same percentage composition or empirical formula, but exhibit different properties. There are two classes; first, those which have the same molecular weight; second, those which have different molecular weights.

The first class is subdivided into *isomeric bodies* proper and *metameric bodies*.

Isomeric bodies have the same chemical properties but differ in physical properties. Thus, $C_{10} H_{16}$ is the symbol for the volatile oils of lemon, juniper, etc., differing only in odor and their action on polarized light. Again, calcium carbonate crystallises in two fundamentally distinct forms, as calcite and as aragonite. These differences are probably due to variations in the grouping of the molecules and not to ...ls, to differences in the molecules themselves.

... they enter.

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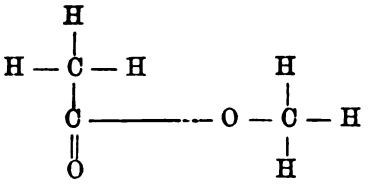
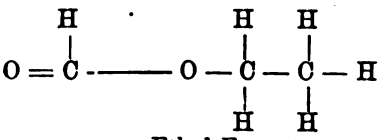
Metameric bodies differ in their chemical properties. Thus, methyl acetate and ethyl formate have the same molecular formula, $C_3 H_6 O_2$, but are entirely different substances. This is probably due to differences of structure in the molecules, which, from their chemical reactions, are known to be,



Methyl Acetate.



Ethyl Formate.

The second class consists of *polymeric* bodies, Their molecular weights are multiples of each other. Thus the paraffins form a series having the composition $Cn\ H_{2n+2}$. Acetic ether, $C_4 H_8 O_2$ is polymeric with aldehyde, $C_2 H_4 O$.

In case of elements showing such relations, the term *allotropism* is applied. Thus, there are two allotropic forms of phosphorous and three of carbon (diamond, plumbago, charcoal). These allotropic forms are probably polymeric, the diamond molecule probably differs from the charcoal molecule in containing a larger number of carbon atoms. Oxygen and ozone differ in the same way, the oxygen molecule is $O_2$, the ozone molecule is $O_3$. The sulphur vapor molecule at a temperature a little above the boiling point of sulphur is $S_6$, at 860° C only $S_2$. The molecule of nitrogen tetroxide at a low temperature is $N_2 O_4$ at a high temperature $NO_2$.

**Chemical Affinity.** — The force by which new compounds are formed is called chemical affinity. This force acts only at insensibly small distances, hence, the closest proximity of the particles of the different substances reacting on each other is necessary. Cohesion opposes combination by preventing this proximity; hence, the solid state is not generally favorable for its action. In gases, the comparatively great distance between the molecules prevents this proximity, unless the pressure to which the gases are subjected be increased above the normal; hence, the gaseous state is not generally favorable for its action. In liquids, the cohesion is so slight as not to prevent this close proximity of the particles of the reacting substances, and the distance between the molecules is comparatively small; therefore, the liquid state, solution or fusion, is the most favorable for its action.

The force of affinity between different substances varies greatly, and it seems to be greatest between bodies most opposed to each other in chemical properties, as acids and bases, for instance. It is influenced to a great extent by external circumstances. The following are the most important of these external circumstances.

*Difference of Temperature.* — At a temperature near the boiling point, mercury combines with oxygen, $Hg + O = Hg O$. At a higher temperature it loses this

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affinity for the mercuric oxide thus formed, and the compound is again decomposed, $Hg\,O = Hg + O$.

*Difference of Solubility or Volatility.* — When two substances, which, by a chemical reaction, are capable of forming an insoluble compound (or a compound less soluble than the original compounds), are brought together in solution, the reaction generally takes place, and the insoluble (or less soluble) compound is precipitated.

When two substances, which, by a chemical reaction, are capable of producing a volatile one, are heated together, the reaction generally takes place and the volatile compound passes off as a gas.

These are the *Laws of Berthollet*, discovered in 1799.

When calcium chloride and ammonium carbonate are brought together in solution, since by double decomposition an insoluble compound (calcium carbonate) *can* be formed, it *will* be

$$Ca\,Cl_2 + (NH_4)_2\,CO_3 = Ca\,CO_3 + 2\,NH_4\,Cl.$$

If, now, these resulting substances, calcium carbonate and ammonium chloride, in the solid state, be heated together, the inverse reaction will take place. A volatile compound (ammonium carbonate) *can* be formed and therefore it *will* be

$$Ca\,CO_3 + 2\,NH_4\,Cl = Ca\,Cl_2 + (NH_4)_2\,CO_3.$$

Calcium, which, in the first case, left the chlorine to combine with the radical $CO_3$, in the second case leaves this radical to combine with chlorine.

*Difference of Atmosphere.* — When iron filings are heated to redness in a tube, and vapor of water passed over them, the iron combines with the oxygen of the water and hydrogen gas escapes,

$$3\,Fe + 4\,H_2\,O = Fe_3\,O_4 + 8\,H.$$

If, now, the iron oxide formed is heated in a tube and hydrogen passed over it, the inverse reaction takes place; the iron loses its affinity for oxygen and the oxide is reduced,

$$Fe_3\,O_4 + 8H = 3\,Fe + 4\,H_2\,O.$$

Apparently, this difference is due to the difference in the atmosphere in the tube, an atmosphere of water vapor offers less resistance to the passage of hydrogen than to the passage of its own vapor, and an atmosphere of hydrogen offers less resistance to the passage of water vapor than to that of its own molecules. These slight differences determine the reaction.

*Nascent State.* — Compounds or elements just being produced or liberated from

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combination, said to be in the *nascent state*, are very energetic in their action. This effect of the nascent state, is, very likely, due to the fact that the reagent is generally liberated in the gaseous form from solids or liquids, and, before it assumes the perfect gaseous state, its molecules must be in almost as close proximity as those of the solids or liquids from which it is derived : hence its more energetic action. Thus, the chlorine just liberated, when gold is placed in nitro-muriatic acid, combines with the gold : whereas, chlorine, under ordinary circumstances, has no such action. Again, nitrogen and hydrogen do not combine under ordinary circumstances; but, when both are just being liberated in the putrefactive decomposition of animal and vegetable matter, they combine and form ammonia.

*Disposing or Concurring Affinity.* — Certain substances *dispose* others to unite, apparently in anticipation of the affinity they will have for the compounds formed. Thus, silver has very little affinity for oxygen ; but, when it is heated with silica, an acid oxide, it will combine with the oxygen of the air, forming silver oxide, which then combines with the silica to form silver silicate. The silica could not combine with the silver, therefore it *disposed* the silver to oxidise in order that it might combine with the oxide formed.

**Thermo-Chemistry.** — Chemical combination always produces heat. The atoms of the bodies concerned, rush upon each other, urged by the attractive force we call chemical affinity, acquiring thus an enormous moving power. This onward motion is arrested when the chemical union takes place, and is converted into the molecular motion we call heat. The quantity of heat due to any given chemical action is fixed and definite. The heat absorbed in the decomposition of a compound is equal to the heat evolved in its formation.

Chemical changes are usually accompanied by physical changes, such as expansion and contraction, changes of state, and so on, which also involve loss or gain of heat, and, therefore, complicate the result.

In all cases the effects are conformable to the principle of the conservation of energy.

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## SECTION 2.

### Chemical Analysis.

There are two methods of research in Chemistry — *Analysis*, in which the compound is resolved into its constituents, and *Synthesis*, in which the constituents are made to unite and produce the compound. The former is of much more general application than the latter. The study of these processes is known, in general, as *Chemical Analysis*.

Chemical Analysis is subdivided into two branches, — *Qualitative*, the object of



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which is to determine the nature of the constituents of a compound, *Quantitive*, the object of which is to determine the amount of the constituents of a compound.

A qualitative examination is made, either to determine the presence of any particular substance, or to determine all the constituents of a compound or mixture. The object of qualitative analysis is attained by converting the unknown constituents of a body into known forms, from which the presence of the constituents may be inferred. Thus, if silver nitrate be added to a solution of common salt (sodium chloride) the chlorine appears in a new form in combination with silver, easily recognized by its white, curdy appearance, and solubility in ammonia. The qualitative examination always precedes the quantitative, both because it is necessary to know what the constituents are, and because the constituents present determine the best method to be pursued in the quantitative estimation.

The object of quantitative analysis is attained by two principal methods, — the *Gravimetric* method, or analysis by weight, and the *Volumetric* method, or analysis by volume.

**The Gravimetric Method** has for its object the conversion of the known constituents of a substance into forms of known composition, and which are capable of being weighed exactly. The new forms may be either educts or products.

Thus, to determine the amount of carbon dioxide in calcium carbonate, we may heat 10 grammes to a white heat and determine the loss in weight. This must be the weight of the carbon dioxide evolved, provided no volatile impurities are present.

$$Ca\,CO_3 = Ca\,O + CO_2.$$

In this case the new form, carbon dioxide, is an educt as it existed in the original substance.

Again, to determine the amount of copper in blue vitriol, we may dissolve 10 grammes in water, add hydrogen sulphide, ignite the precipitate in a stream of hydrogen and weigh —

$$2\,(Cu\,SO_4 . 5\,H_2O) + 2\,H_2S = 2\,Cu\,S + 2\,H_2SO_4 + 10\,H_2O.$$

$$2\,Cu\,S + 2\,H = Cu_2S + H_2S.$$

Suppose we find the weight to be 3 grammes. Then, to calculate the amount of copper in it

$$158.6 : 126.6 :: 3.00 : y = 2.4 \text{ grammes Cu.}$$

In this case the new form, cuprous sulphide, is a product, since it was formed by the addition of sulphuretted hydrogen, and subsequent ignition in hydrogen.

The gravimetric method is subdivided into analysis in the "wet way" and analysis in the "dry way." In the former, the reagents are in solution and act in

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that form on the substance to be analyzed ; in the latter, both substance and reagents are in the solid form and their combination is effected by means of heat. In the different steps of an analysis both methods are generally used.

Assaying, not properly analysis, is a form of analysis in the "dry way," its object being to imitate, on a small scale, metallurgical processes for obtaining the metals from their ores, and to determine approximately the yield of an ore.

Substances are separated from solution as precipitates by means of reagents, and in quantitative analysis they should always be *separated* in their most insoluble forms, and *determined* in the forms in which they are least liable to change under the influence of heat or air.

The form in which one substance is separated from another is not always the same as that in which it is determined. Thus, in the determination of copper, above, the copper is *separated* as cupric sulphide ; but this can not be dried without partial oxidation, yielding a variable mixture of oxide and sulphide. Hence, it is *determined* as cuprous sulphide, which is unchanged in a current of hydrogen.

Bodies may be separated and determined in three ways. 1, By *direct analysis*, in which one body is rendered insoluble while another remains in solution, or one body is volatilized while the others remain behind, etc. 2, By *indirect analysis*, in which the bodies are not separated, but certain changes are produced from which the quantities of the bases or acids present may be calculated. 3, By *difference*, in which the sum of the weights of two bodies is obtained, and one of them is separated and its weight determined. The other is then determined by taking the difference of these two weights.

**The Volumetric Method** has for its object the conversion of a substance from one definite state to another by means of a liquid of known power of action, and the accurate determination of the exact point when the conversion is complete.

Thus, if a solution of potassium permanganate be added drop by drop to an acidified solution of ferrous sulphate, the red color of each drop of the permanganate gradually disappears as it is added, until, finally, a drop colors the whole solution pink, this marks the completion of the test. The iron has been converted from the ferrous into the ferric state by the oxidising power of the permanganate.

In volumetric analysis, measurement is made by means of a solution of the reagent, the chemical power of which is accurately known, called a *standard solution*. Standard solutions are often constructed so that 1 c. c. = 0.01 grm. of the substance sought. They are titrated, i. e., quantitatively tested for the amount of pure substance they contain, by means of standard solutions of the substance for the determination of which they are to be used.

*Normal Solutions* are standard solutions which contain in the litre a number of grammes of the substance equal to its atomic or molecular weight. Solutions of one-tenth, one-hundreth, etc., of this strength are called *Decinormal, Centinormal*, etc., solutions.

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In the preparation of normal solutions from crystallized salts, it is necessary to consider the water of crystallization, since this will also be weighed in weighing the salt. Thus, green vitriol contains seven molecules of water of crystallization ; hence, a number of grammes equal to the molecular weight of $Fe\,SO_4 . 7\,H_2O$ must be taken to the litre in order to obtain a number of grammes of iron to the litre equal to its atomic weight.

The normal temperature for the preparation and use of standard solutions is 16° C or about 60° F.

The determination of a substance may be effected volumetrically by three principal methods.

1. By saturation, as in the case of acids or alkalies.

2. By an oxidising or a reducing agent. The principal oxidising agents are potassium permanganate, potassium bichromate, and iodine. The principal reducing agents are ferrous and stannous compounds and sodium hyposulphite.

3. By precipitation, as when silver is precipitated from solution by means of common salt.

The end of the operation is made apparent to the eye by various means, such as the appearance of a distinct color, the change in color of litmus added to the solution, a precipitate ceasing to form, etc. Sometimes it is necessary to use an *indicator* to determine, usually by the color produced, the exact point of saturation. Thus, in the estimation of chlorine by means of a standard solution of silver nitrate, potassium chromate is added as an indicator. As soon as the reddish tinge due to silver chromate remains permanent, all the chlorine has been precipitated as silver chloride.

### *Apparatus and Operations.*

Before beginning an analysis, an exact plan of procedure, in which all the chemical relations are considered, is prepared, and, during the process, the results at every step are accurately noted on paper.

**Selection of the Sample.** — The selection of the sample depends somewhat upon the object of the analysis. If the investigation is a scientific one, such as the determination of the constitution of a mineral, the sample selected must be perfectly pure, all gangue and impurities being carefully removed ; but, if the investigation is a technical one, such as the determination of the amount of iron present in an iron ore, the sample selected must simply correspond to the average quality of the ore.

Before breaking up a sample, it is examined to determine its mineralogical character, either by its external appearance or by its reactions when tested before the blowpipe.

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**Mechanical Division.** — Chemical affinity acts only at insensibly small distances; therefore, the action between a liquid and a solid is only a surface action. By finely dividing the solid, the extent of surface exposed to the liquid, and consequently the chemical action, is increased.

To effect this division, large pieces are generally first reduced to course powder in an iron or steel mortar, or are wrapped in writing paper and reduced to powder on an anvil by means of a hammer. Salts and substances of no considerable degree of hardness are pulverized in glass or porcelain mortars (*Fig.* 1, *Pl. I*). The harder minerals, especially when but small portions are available, are placed in the cylindrical chamber B of a diamond mortar (*Fig.* 2, *Pl. I*), and are pulverized by striking repeated blows on the pestle with a hammer. The division is completed by rubbing the powder fine in an agate mortar (*Fig.* 3, *Pl. I*). In the use of mortars great care must be taken to keep them clean. Iron mortars are cleaned by pulverizing sand in them or by rubbing with a pestle of pumice; glass and porcelain mortars are cleaned with a towel. The material of the mortar must be considerably harder than the substance to be pulverized.

After pulverization to a coarse powder the sampling takes place, it consists in spreading the ore out in the form of a circle, dividing this circle into quarters, selecting one of the quarters, spreading it out as before, quartering again, and so on until a sample of the proper size is obtained. Ores for assay are generally pulverized until they pass through a sieve with eighty meshes to the inch, the siftings are then mixed on glazed black paper. In case the ore contains metallic particles which cannot be pulverized, the powdered ore is separated by means of the sieve into siftings and metallic residue. The siftings are sampled as before, the residue is tested as a whole.

In certain cases a greater degree of pulverization than that obtained in the agate mortar is required, as in the case of minerals insoluble in acids; these must be reduced to an impalpable powder. The operations described are completed, in case the substance is not attacked by water, by a process called *levigation*, which consists in moistening the fine powder in the agate mortar and triturating the paste until all crepitation ceases. It is then transferred to a beaker and the finer particles are obtained by a process called *elutriation*, which consists in adding distilled water, stirring, allowing to stand for a minute and decanting; the process is repeated. The decanted water will deposit the fine particles it holds in solution in a few hours; the water is then decanted, the residue dried. This method is not applicable in case the coarser and finer particles are liable to differ in composition.

**Weighing.** — The quantity of solids is usually determined by weight, and the value of the results of an analysis depends, to a great extent, upon the accuracy of this operation.

*The Balance* — The analytical balance, (*Plate II*), consists of a beam, supports, scale pans, index and scale. The supports and the axes of suspension of the beam and scale pans are made of steel or agate, the latter are knife-edges.

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In the form here represented the beam has three knife-edges, one in the middle, which, when in use, rests on an agate surface set in the top of the brass support, and one at each end, on which rests the agate surface set in a frame from which the scale-pans are suspended. The knife-edges are all in the same plane.

At one extremity of the beam, a small rod W, provided with a screw-thread, is attached, on which a weight P can be run in or out. The beam is graduated on the other side by dividing its half length into ten equal parts and subdividing these tenths. On this beam, the rider (*Fig.* 4, *Pl. I*), is used; it consists of a piece of platinum wire bent so that it will rest on the beam in a vertical position; it has a loop on top so that it can be removed or placed in position, by means of a hook attached to the rod R which has a motion of rotation about its own axis, and one of translation in the direction of its length.

The index I is screwed into the bottom of the frame, it has a small weight attached which may be moved up and down and can be secured by a set screw.

When the balance is to be used, the middle knife-edge and the frames are lowered to their supports by turning the screw N. The scale-pans would swing free were it not for the two arresting screws *a* attached to the horizontal bar E, the pads of which touch the bottoms of the scale-pans. The inclination of these arms can be regulated by a screw *g*. These arresters are removed from the scale-pans by pushing in the rod A, which can be prevented from springing out again by turning it to the right or left. When the balance is no longer required the screw N is turned in the opposite direction, raising the middle knife-edge, whereby the supports CC on the bar B receive corresponding projections on the beam and lift it, at the same time the V shaped projections on B lift the frames resting on the knife edges at the end of the beam.

L is a level, SS are leveling screws.

The capacity of the balance should be about 100 grammes.

*Theory of the Balance.* — The *sensibility* of a balance is directly proportional to the amount of deviation of the beam from its horizontal position, due to a given difference in the weights acting at the points of suspension of the pans. The *stability* of a balance is directly proportional to the force tending to restore the beam to its horizontal position when disturbed.

To determine expressions for sensibility let O, (*Fig.* 5, *Pl. I*), be the centre of oscillation of the beam, E E′ the points of support of the scale-pans at equal distances from O. Suppose equal weights, each equal to P′, to act at E and E′, then the total weight 2 P′ may be conceived as acting at C, the middle point of the line E E′. Let P be the weight of the beam. This weight may be considered as acting at the centre of gravity of the beam, G, which, since O C is perpendicular to E E′, and the beam is symmetrical with respect to it, must be on this line O C. The beam will therefore remain horizontal. Now let some additional weight *p* (small as compared with P and P′) act at E. The beam will come to rest in some

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position inclined at an angle, say $\theta$, to its original horizontal position, and the forces acting on the two sides of the centre of oscillation of the beam must be in equilibrio. The sum of their moments with respect to this axis of oscillation must therefore be equal.

$$2\,P' \,.\, OB + P \,.\, OA = p \,.\, ON = p\,(BN - BO).$$

Substituting for OB, OA, and BN, their respective values in terms of $\theta$, OC′ Sin $\theta$, OG′ Sin $\theta$, C′ E Cos $\theta$, we have

$$2\,P' \,.\, OC' \,.\, \text{Sin}\ \theta + P \,.\, OG' \,.\, \text{Sin}\ \theta = p \,.\, C'\,E \,.\, \text{Cos}\ \theta - p \,.\, OC' \,.\, \text{Sin}\ \theta.$$

$$\text{Tan}\ \theta = \frac{\sin\ \theta}{\cos\ \theta} = \frac{p \,.\, C'\,E}{(2\,\Gamma' + p)\,OC' + P \,.\, OG'}.$$

For small values, Tan $\theta$ varies very nearly as the angle of deviation $\theta$; hence, this is the equation of sensibility, and we see that the sensibility increases directly as the length of the beam, and nearly inversely as the weight of the beam and of the load, and also nearly inversely as the distance of the centre of gravity of the beam and of the middle point of the line joining the points of support of the scale-pans, from the centre of oscillation of the beam.

The expression for stability is —

$$(2\,P' \,.\, OC' + P \,.\, OG')\ \text{Sin}\ \theta.$$

If C′ coincide with O the expression for sensibility becomes Tan $\theta = \frac{p \,.\, OE}{P \,.\, OG}$, which depends only on $p$. The expression for stability becomes P . OG′. Sin $\theta$, which is constant. Hence, the centre of oscillation of the beam and the points of support of the scale-pans should be in the same right line.

A balance should be so adjusted in its length, strength, weight, and relative position of the centres of suspension and gravity, as to combine the exact degrees of sensibility, stability, or quickness, and capacity for bearing weights which its special employment requires.

*Adjustments and Tests.* — There are three principal adjustments.

1st. The supports of the beam are leveled.

2nd. The beam is lowered to its support, and the rod A gently pushed in and turned. If the index I swings equally on both sides of the zero mark, the scale-pans are adjusted; if not, they are balanced by running the weight P in or out.

3rd. The arms $a$ are adjusted so that when the index is at zero the pads shall just touch the bottom of the scale-pans.

In order to test a new Balance, it is first accurately adjusted as explained, and the following tests are then applied —

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1st. A milligramme weight is placed in one scale: it should turn the beam distinctly — a good balance will turn with $\frac{1}{10}$ milligramme.

2nd. Both scales are loaded with the maximum weight the construction of the balance will admit of, the balance is accurately adjusted, and a milligramme added to the weight in one scale: the beam should turn to the same extent as in the first test.

3rd. The balance is accurately adjusted and both scales are equally loaded with about 50 grammes each; the balance is again adjusted by the addition of small weights. The loads are then interchanged and equilibrium should be maintained.

4th. The balance is accurately adjusted; the beam is arrested and again set in motion and the process repeated several times: it should resume its original equilibrium.

The Balance should never be moved from its appointed place. It should not be in a position where it is liable to be exposed to acid fumes; therefore, in large laboratories there is a separate room in which the weighing is performed. The Balance is kept dry by placing a vessel containing a little concentrated sulphuric acid inside of the case.

*The Weights.* — Grain weights are still used by some English and American chemists, but most men of science of all nations have adopted the gramme weights, or Metric System, because it is a decimal system, and, on account of the facility with which weights are converted into volumes and the reverse.

A set of weights usually ranges from one milligramme to fifty grammes. The weights should be kept in a well-closing box, with a separate compartment for each weight. Those from one gramme upwards are best made of brass *gilt*, with a handle on top, those below one gramme should be of platinum in the form of flat squares, with a corner bent up for holding in the forceps. All the weights should be tested when first received, by balancing them against each other in various ways.

*The Process of Weighing.* — There are two methods of weighing: the *direct* method, in which the substance is placed on one scale and the weights on the other; and the method *by substitution*, in which the substance is placed on one scale and is counterpoised accurately, it is then removed and weights are substituted for it till equilibrium is restored. The substance is invariably placed on one and the same scale, most conveniently on the side opposite to that on which the beam is graduated.

The balance should be leveled and in adjustment before beginning to weigh; and, during the process, the case should be left open as little as possible. The beam should always be lifted when placing or removing substances or the larger weights, using the arrester only when slight changes are made. The beam should never be lifted nor the arrester used, except when the index is near the centre of the scale.

The weights should never be touched with the fingers, but always handled with pincers provided for that purpose. In ascertaining the weight of a substance the weights should be tried in a systematic way. A weight is selected about equal to

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the substance and tried; if too great, the next smaller one is substituted, and so on until one is found equal to or less than the substance. If less, the next smaller one in the set is added, if this is too great, the next smaller is substituted for it, and so on to the smallest weight, using the rider for those under ten milligrammes. The half beam is divided into ten equal parts, and, as the weight of the rider is one centigramme, each division corresponds to one milligramme. These divisions are further subdivided so that $\frac{1}{10}$ milligramme is easily read. The exact weights are carefully entered in the note-book. Whenever a weight greater than one centigramme is placed or removed, the balance is arrested.

The amount of a substance required for quantitative analysis depends upon the nature of its constituents. One to three grammes is usually sufficient; but, for the estimation of constituents present in minute proportions, 100 grammes may be required.

Substances should never be placed directly upon the scale-pans, but should be weighed in appropriate vessels — never on paper, as this is liable to absorb moisture. If but one portion of a substance is to be weighed, two watch-glasses of the same size, (*Fig.* 6, *Pl. I*), with a clamp to hold them together, or a platinum crucible and lid, are weighed; the substance is then introduced and the whole weighed: the difference in the two weighings is the weight of the substance. In case the substance is to be treated in some vessel other than that in which it is weighed, it is generally better to fill a small tube, closed at one end (*Fig.* 7, *Pl. I*) with the substance, weighing the whole, then shaking out the required quantity into the proper vessel and weighing again. If several quantities of a substance are required, they may be shaken out in succession, weighing the tube after each time. Hygroscopic substances must be weighed in close vessels; liquids, in small bottles with glass stoppers. Vessels should always be weighed at about the temperature of the air.

In using a double filter, the difference in weight of the two filters is ascertained, and, in weighing the residue or precipitate on the filter, the lower filter is used to counterpoise the upper. The difference in weight of the filters is added to or subtracted from the result, according as the upper is the lighter or heavier.

When the weighing is completed the substance is removed, the weights, pincers and box-cover replaced, the rider removed and the case closed.

**Measuring.** — This process is generally confined to gases and liquids. For measuring *gases* graduated tubes of strong glass, sealed off round at one end are used. The gases are generally collected in these tubes over a mercurial trough.

For measuring *liquids* two kinds of vessels are used, those graduated for *the contents*, and those graduated for *delivery*. The first includes *measuring flasks*, *graduated measures*, and *cylinders;* the second, *pipettes* and *burettes*.

Measuring flasks, (*Fig.* 8, *Pl. I*), should have well ground glass stoppers, and the graduation line should fall just below the middle of the neck. They are used for mixing standard solutions to a given volume. Graduated measures and cylinders



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are used for measuring liquids for various purposes in the laboratory: they are graduated in ounces or in cubic centimetres, small ones in minims.

Pipettes (*Fig.* 9, *Pl. I*) are of two kinds, those which deliver one certain quantity only, and those graduated to deliver various quantities. The pipette is filled by suction at the upper aperture until the fluid stands above the mark, the aperture is then closed with the fore-finger of the right hand and the fluid is allowed to run out to the mark by lifting the finger slightly. The liquid may then be transferred to any vessel either wholly or in part.

The burette is the instrument most generally employed for measuring liquids in analysis. The best form is Mohrs', (*Figs.* 10 *and* 11, *Pl. I*), with rubber tube and spring clip for regulating the flow, or better still with a glass stop-cock. To charge the burette, it is filled a little above the zero and the clip or stop-cock opened fully for a moment, so that the liquid may completely fill the point. It is then adjusted in a vertical position and the liquid allowed to drop out to zero. On account of capilarity the surface of the liquid is curved and there is some difficulty in reading accurately; but, by the use of Erdmann's Float, (*Fig.* 12, *Pl. I*) all uncertainties in reading off are avoided. This consists of an elongated glass bulb of smaller diameter than the burette, weighted at the lower end with a globule of mercury, and having a ring at the upper end, by means of which it may be lifted into and out of the burette. A line is cut around its middle, and the coincidence of this line with the graduation marks of the burette is accepted as the true reading. A marble is placed on the open end of the burette to prevent evaporation and the entrance of dust.

**Furnaces.** — The determinations in assaying are made by the direct action of heat and the operations are conducted in furnaces. Various forms of furnaces are used, their construction depending upon the kind of fuel employed. Most laboratories have stationary furnaces; but, for ordinary work, portable furnaces of iron or of clay, iron bound, are inexpensive, convenient and much used. *Fig.* 1, *Pl. III*, represents a crucible furnace principally used for heating sand or clay crucibles containing metals, ores, etc., to be fused. *Fig.* 2, *Pl. III*, is an Assay Furnace which may be used for the same purpose, but is principally used in the roasting and scorification of ores and in the cupellation of gold and silver ores. These operations are conducted by placing the vessels containing the ore in the muffle seen through the main opening, the current of air for oxidation being regulated by opening or closing this opening. The fuel used is charcoal, this is placed around the muffle, the draught being regulated by the openings below.

**Lamps.** — These are used in the processes of analysis requiring the application of heat, and are either spirit lamps or gas lamps.

There are two kinds of spirit lamps, the simple spirit lamp of glass or copper, (*Fig.* 3, *Pl. III*), and the spirit lamp of double draught, involving the principle of

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the argand burner, the rate of combustion being increased by supplying air inside of the flame as well as outside. *Fig.* 4, *Pl. III*, represents such a lamp, called a *Berzeluis lamp*, with the necessary apparatus used with it.

Bunsen's, (*Fig.* 5, *Pl. III*), is the best form of gas lamp. The gas is supplied by a flexible tube and enters at the box *g*, where it is mixed with atmospheric air entering by a number of holes at the top of the box. The gaseous mixture passes up the tube *a* and is inflamed at the top, where it burns as a *solid* flame of great heating power. In place of the box with holes, there is now, usually, a perforated ring, movable around the tube, by means of which the supply of air may be regulated.

**Drying.** — Most solids absorb variable quantities of water, and, in order to obtain them in a definite state, it is necessary to dry them previous to analysis. This water is held mechanically and is usually called *hygroscopic moisture* to distinguish it from *water of crystallization* which is chemically combined, and is essential to the crystalline forms of compounds.

Efflorescent substances, or those which lose their water of crystallization by exposure to the atmosphere at ordinary temperatures, are generally dried by pressing the pulverized salts between thick layers of fine white blotting paper.

Substances not altered by exposure at ordinary temperature, but losing combined water at 100° C., must be dried at ordinary temperatures. They are finely pulverized, the powder placed in a thin layer in a watch-glass, and the latter placed in a chamber in which the air is kept dry by means of some substance which has a great affinity for water, as sulphuric acid, calcium chloride, zinc chloride, quick lime, etc. The simplest form of such an apparatus is represented in *Fig.* 6, *Pl. III*, and is called a *Desiccator* or *Exsiccator*. The operation may be hastened by exhausting the air by means of an air-pump.

Substances which completely lose their moisture at 100° C. but suffer no other change, are dried in the *water-oven*, with or without the aid of a current of dry air. The *water-oven*, (*Fig.* 7, *Pl. III*), is made of copper, with double walls for enclosing the water to be boiled. A thermometer indicates the temperature of the water or of the air in the chamber. The substance to be dried is placed on double watch-glasses, laid one within the other, which are placed in the oven and the door is closed. In removing the substance, the upper glass is covered with the lower and the two are held together by a clip. If the water in the oven be allowed to evaporate completely while the heat is being applied, the oven is liable to be ruined by the fusion of the solder.

The method of drying in a current of air is represented in *Fig.* 8, *Pl. III*, in which *a* contains sulphuric acid, *c* is the drying tube, containing the substance, which is first weighed with the substance, then placed in the water-bath A, and the connections made. *d* is the aspirator, filled with water; by opening the stop-

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cock *e*, air will pass into *b* to be dried by the sulphuric acid, thence it will pass over the warm substance, drying it, and into the aspirator to replace the water which has passed out.

Substances which retain their moisture at 100° C. but are decomposed at a red heat, are dried by heating them in air-baths, oil-baths, etc. The water in a water-oven may be replaced by solutions of various salts or by oil, substances which boil at a higher temperature than water. The following substances may be used.

| | |
|---|---|
| Sodium Chloride, saturated solution, boils at | 108.4° C. |
| Strontium Chloride, saturated solution, boils at | 117.8° |
| Glycerin, boils at | 290 ° |
| Linseed Oil, may be heated up to | 300 ° |
| Olive Oil, may be heated up to | 300 ° |
| Paraffin, may be heated up to | 315 ° |

The air-bath, (*Fig.* 9, *Pl. III*), is constructed of sheet copper; heat is applied by a lamp to any temperature, indicated by the thermometer *d*. To heat at a fixed and constant temperature by means of gas, Bunsen's attachment is used. The gas enters at *a*, before passing to the burner, and, if the temperature has a tendency to rise above that for which it is set, the mercury in the bulb of the regulator rises by expansion and partially cuts off the supply of gas. When the temperature begins to fall below the point fixed the mercury recedes by contraction due to the cooling and the supply of gas is increased.

Substances which will bear a red heat without alteration are best dried by simply heating in a platinum or porcelain crucible.

Before weighing, the heated vessels are allowed to cool under a desiccator, and the drying is not considered complete until the substance ceases to lose weight.

The estimation of the water contained in a substance is made after weighing the sample. In certain cases the hygroscopic moisture is to be determined, as in the analysis of gun powder; in this case no previous drying can take place. But in case combined water is to be determined, the substance is previously dried to remove hygroscopic moisture.

The estimation of water may be effected in two ways, — by determining the loss of weight due to the expulsion of the water, and by weighing the water expelled. The former may be performed by any of the methods described, according to the nature of the substance. The latter is performed by heating the substance to a red heat and condensing the water in a receiver, partly physically and partly by the agency of some hygroscopic substance. The increase in the weight of the condensing apparatus represents the quantity of water expelled.

**Solution.** — Solution is the result of a weak kind of chemical affinity between the substance dissolved and the solvent, resulting in a change of state in the former

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from solid to liquid. The solution may be *simple*, when no definite combination takes place, or *chemical*, when the solvent and the substance dissolved combine chemically. Thus, sugar dissolves in water in all proportions up to a certain point, producing a simple solution, and, if the water be evaporated, all the sugar will remain; whereas zinc dissolves in hydrochloric acid, producing a chemical solution, and, if the liquid be evaporated, zinc chloride will remain.

A simple solution is said to be *saturated* when the solvent has received as much of the dissolved substance as it can retain. The solubility of a salt generally increases with the temperature, but the solubility of common salt is nearly the same at all temperatures, and calcium and magnesium hydrate are more soluble in cold than in hot water.

In order to facilitate the action of chemical agents, it is generally necessary to obtain the substance to be analyzed in a state of solution. The ordinary solvents for this purpose are water, acids, and alkalies. Substances insoluble in these require previous decomposition by fusion. It is not always necessary to dissolve the substance as a whole, several solvents may be used to separate the constituents; thus, in the case of gunpowder, the nitre may be dissolved by water, the sulphur by carbon bisulphide, the charcoal remaining undissolved.

Solution is effected in beakers, flasks, and dishes, with or without the assistance of heat. Solution is promoted by agitation or by stirring with a glass rod. The heating may take place by the direct application of the flame, by supporting the vessel on wire gauze and applying the heat below the gauze, by heating in a water-bath, or by supporting the vessel on a sand-bath, consisting of an iron dish filled with sand, and applying the heat to the iron dish. To prevent spirting, the heating may take place in a flask placed in a sloping position, or in a beaker covered with a large watch-glass. In cases where the solution is effected by means of concentrated volatile acids, the operation should be conducted under a hood to allow the escape of the acid vapors.

**Crystallization.** — Crystallization is one of the fundamental properties of matter and is closely related to the cohesion of ordinary solidification. Crystals are solids formed by the crystalline force, they are bounded by plane faces, which, when the crystal is perfect, are symmetrically arranged. Substances which do not crystallize are said to be *amorphous*, examples of which are opal, limonite, charcoal, etc.

Crystallization may take place from the state of vapor, as when sulphur vapor condenses to flowers of sulphur; or from the liquid state, either that of fusion, as when melted cast iron solidifies, the crystalline structure produced being indicated in the fracture, or that of solution, as when a solution of common salt is evaporated, or a hot concentrated solution of alum is allowed to cool, or two substances in solution, as barium chloride and sulphuric acid, produce an insoluble one by double decomposition; or it may even take place from the solid state, as in the crystallization of steel bars subjected to constant vibration.



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The most common method of obtaining crystals is from a state of solution, either by evaporation, or by cooling a hot concentrated solution. The slower the rate of conducting the process the larger and more perfect will the crystals be. The principal objects of crystallization, are to obtain a substance in a solid form, or to separate it from other substances present in a solution.

**Evaporation.** — Evaporation is the transformation of a liquid into a gas, and is used to separate volatile liquids from less volatile, or from fixed bodies when the residue alone is of importance. Hence, it is one of the methods of converting a substance in solution into a form adapted for weighing. It is also used to concentrate dilute solutions.

The object may be attained by any of the methods of drying, but is usually accomplished by the application of heat. The operation is conducted in evaporating dishes, (*Fig.* 10, *Pl. III*) of porcelain, glass, or platinum, which are heated on a water-bath, steam-bath, sand-bath, or directly by a lamp. The steam-bath, (*Fig.* 11, *Pl. III*), consists of a hemispherical copper vessel, half filled with water which is kept boiling over a lamp; various flat rings adapted to receive dishes of different sizes fit over the top. To exclude dust, the evaporating dish is covered with a sheet of filtering paper or with an inverted funnel; and, to prevent loss, the liquid is never allowed to enter into ebullition.

In case a liquid is to be evaporated to dryness, the operation should be terminated on a water or steam bath, and, if it is required to weigh the residue, the operation is terminated in small platinum vessels 4 to 8 centimetres in diameter. In transferring the fluids from the larger to the smaller vessels, the lip of the former is slightly greased, and the liquid made to run down a glass rod, (*Fig.* 1, *Pl. IV*), the larger vessel is then rinsed with a wash-bottle (*Fig.* 2, *Pl. IV*). The dish should remain covered during the weighing.

**Distillation and Sublimation.** — Distillation is the process by which a liquid is converted into vapor and the vapor is recondensed in the liquid form. The object of distillation is either to separate liquids which rise in vapor at different temperatures, or to separate a volatile liquid from an involatile substance, where the evaporating liquid is of importance. Every distillatory apparatus consists essentially of a retort in which the liquid is heated, of a condenser in which the vapor is cooled and condensed to the liquid state, and of a receiver to collect the distillate. The Liebig form of condenser is represented in the figure of the apparatus used in water analysis; the vapor from the retort passes through a small tube in the axis of the large cylinder to the receiver. Cold water passes from the cistern into the large cylinder, and surrounds this tube and thus cools it condensing the vapor in the interior.

Sublimation is the process by which a solid is converted directly into vapor and the vapor is recondensed to the solid state. Its object is to separate substances of

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different degrees of volatility, as in the sublimation of sulphur, iodine, or ammonium chloride.

**Precipitation.** — Precipitation is the process of forming an insoluble substance in a solution, either by modifying the solvent, as when alcohol is added to a solution of potassium carbonate, or by simple or double decomposition, — the insoluble substance is called a *precipitate.* The object of precipitation is to obtain a substance in the solid form, or to separate it from other substances present in solution.

In qualitative analysis, its principal use is the detection of substances by the characters of the precipitates formed by various reagents.

In quantitative analysis, its object is to separate substances from one another and convert them into forms adapted for weighing. The substance to be precipitated should be converted into its most insoluble form, and when not absolutely insoluble the liquid should be concentrated by evaporation, and its insolubility increased by adding substances like alcohol, ammonium chloride, etc., in which it is insoluble. Precipitation is generally effected in beakers, but when the liquid is to be boiled dishes are used. The formation of precipitates is promoted by stirring and the application of heat.

To determine whether the precipitant has been added in sufficient quantity, the precipitate is allowed to settle and a portion of the clear liquid is taken, some precipitant added, the liquid is warmed, and, after some time, it is observed to see if a precipitate has formed.

Precipitates are separated from the liquids in which they are suspended, either by filtration or by decantation or by both combined.

**Filtration.** — This operation consists in separating suspended impurities from a liquid. In analysis this is generally done by passing the liquid through paper. The filters are prepared by double folding a circular piece of paper with the folds at right-angles, forming a quadrant, which is opened to form a cone and placed in a glass funnel. The paper should not project over the rim of the funnel, should fit accurately, and should always be moistened before filtering. Filtering paper should filter rapidly, retain all precipitates, and contain no inorganic matter soluble in acids or alkalies. Swedish filtering paper is the best. Filtering paper is purified by washing in dilute hydrochloric acid and then removing the acid by washing in water. The precipitate should never more than half fill the filter. In the process of filtration the supernatant liquid is poured on the filter first and always by means of a glass rod (as explained under evaporation), directing towards the sides of the filter. The particles of precipitate remaining in the vessel may be removed by means of a feather or the wash-bottle, or by a proper solvent. The point of the funnel should rest against the upper part of the receiving vessel, (*Fig.* 3, *Pl. IV*).

To accelerate the process of filtration, suction is resorted to. The lower part of

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the filter is set in a cone of platinum foil to prevent its breaking, and the whole placed in a funnel, the funnel is fitted into a hole in a rubber stopper projecting some 8 centimetres; into the other hole of the stopper is fitted a short tube bent at right angles, not projecting beyond the stopper inside. The stopper is fixed air-tight into a flask, and suction applied to the outer end of the bent tube, by means of an aspirator or a hydraulic air-pump.

**Decantation.** — This operation consists in simply pouring off the supernatant liquid from a precipitate after subsidence. It is resorted to instead of filtration when the precipitate subsides rapidly and completely. Heat, agitation, or the addition of some reagent, is often necessary to promote the complete subsidence of the precipitate. The precipitate is washed completely with fresh quantities of liquid until no trace of a dissolved substance can be detected in the last rinsings.

The best method is a combination of the two operations just described. The precipitate is allowed to subside, the supernatant liquid is poured on the filter, the precipitate is stirred up with some of the washing liquid, allowed to subside again, and so on. The precipitate is then transferred to the filter and the washing completed with the wash-bottle.

**Washing.** — This is effected by means of the wash-bottle, (*Fig.* 2, *Pl. IV*), its object being to remove from a precipitate the last traces of the liquid in which it was formed. The tube $a$ of the wash-bottle is drawn out to a fine point. By blowing into the other tube, a fine jet of water is expelled through $a$, and with this the precipitate is washed. It is best to use hot water when possible, in this case the wash-bottle must be provided with a wooden handle. Fresh wash-water should never be added to the filter till the old has run through. Care must be taken to wash well the upper part of the filter and not to produce canals in the precipitate.

The proper washing of the precipitate is most important. It should not be considered complete until all soluble matter has been removed, and this fact is generally ascertained by slowly evaporating a drop of the last washings upon a platinum knife and observing if a residue is left, or by applying proper chemical tests.

After the washing is concluded and the water has run off, the filter containing the precipitate is taken off the funnel, placed upon warm blotting-paper, then dried (usually between watch-glasses) and weighed. Sometimes it is necessary to dry on the filter. In all cases the filter is weighed with the precipitate, hence it should always be weighed previous to use.

**Ignition.** — This process serves to separate volatile substances from less volatile or from fixed bodies in cases where the residue alone is of importance. Sometimes it is used to modify the state of a body, or to determine the character or detect the presence of a substance by its behavior during ignition. It is effected by the

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application of a high heat, the temperature required depending upon the nature of the body. Usually a red heat applied for five minutes is sufficient.

Ignition is performed in crucibles, which are of porcelain or platinum in analytical experiments. The latter are preferred. Certain precautions are necessary in the use of platinum crucibles. They should not be used for treating substances liable to evolve chlorine; nor hydrates, nitrates, or cyanides of the alkalies; nor metals or metallic sulphides; nor easily reducible metallic oxides; nor organic salts of the heavy metals; nor phosphates in presence of organic matter. Platinum crucibles must never be set, while hot, on a metal with which the platinum is liable to alloy itself. They should not be exposed directly to a charcoal fire, but should be enclosed in another crucible of sand or clay when so used. They may be cleaned by rubbing with moist sea sand, the grains of which are all rounded, or by ignition, or by sprinkling acid potassium sulphate or borax over them during ignition.

Platinum crucibles are generally heated on platinum wire triangles (*Fig.* 4, *Pl. IV*); they should not be cooled too suddenly as they are liable to crack. In ignition, precipitates must always be thoroughly dried before exposure to a red heat. As it is impossible to separate the precipitate completely from the filter, the latter is also ignited, and the weight of its ash subtracted from the total weight. The quantity of ash yielded by filters of the same size and same variety of paper, is determined by burning ten of them in a crucible and igniting until all the carbon is consumed, then weighing the ash and dividing by ten.

There are two methods of ignition of precipitates, — ignition of the precipitate with the filter, and ignition of the precipitate apart from the filter.

The first method is resorted to when there is no danger of a reduction of the precipitate by the carbon of the filter. The dry filter with the precipitate is removed from the funnel and its sides gathered together at the top to prevent loss; it is placed in the crucible, the crucible is covered, and a very gentle heat is applied. In case the precipitate is easily detached, the bulk of it is placed in the crucible and the folded filter laid over it. When the filter is charred, the cover is removed, the crucible placed obliquely (*Fig.* 5, *Pl. IV*), and a stronger heat applied until complete incineration of the filter is effected. The lid is replaced and a red heat applied; the crucible is then allowed to cool a little, is removed by means of a pair of platinum-pointed tongs, placed in a desiccator, allowed to cool, and weighed.

The second method is resorted to in case a reduction of the precipitate by the carbon of the filter is apprehended, or, in case the ignited precipitate is required for further examination, which the presence of the filter might embarrass. The crucible is placed upon a sheet of glazed black paper; the dry filter with the precipitate is taken out of the funnel, gently pressed together over the glazed paper to detach the precipitate; the latter is then shaken into the crucible, and the filter pressed

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and rubbed to separate the precipitate as completely as possible. The particles on the glazed paper are also poured into the crucible. The filter is cut up over the glazed paper with a pair of scissors, into some ten pieces; the lid of the crucible is heated to redness and one after another of the pieces incinerated on it. The crucible with the precipitate is ignited, and towards the end of the operation the lid containing the filter ash is put on. The filter may also be incinerated by winding one end of a platinum wire spirally about it, and burning it over a crucible placed on a porcelain plate. The ash is added to the contents of the crucible and the latter is ignited as before.

**Calcination and Roasting.** — These are modifications of the process of ignition, the terms applying more especially to certain processes in assaying.

Calcination, is simple heating of a substance, its main object being to drive off water. In assaying it is conducted in crucibles made of graphite, clay, sand, etc. (*Fig.* 6, *Pl. IV*).

Roasting, is heating with free access of air, its object being to effect oxidation, thereby ensuring the elimination of sulphur, arsenic, antimony, etc. Open flat dishes are employed, called roasting dishes, (*Fig.* 7, *Pl. IV*), made of a mixture of sand and clay. The operation is performed in these dishes in the muffle of an assay furnace, the temperature being raised gradually, with constant stirring, and a good draft of air being secured.

**Fusion.** — Fusion is the conversion of a solid into the liquid state by the application of heat. Its object in analysis is to effect the combination or the decomposition of bodies, the liquid state being the most favorable for chemical action. It is conducted in porcelain or platinum crucibles. This process is especially required for the analysis of sulphates of the alkaline earths, and for many silicates and aluminates. The fluxes commonly used are barium hydrate, acid potassium sulphate, and a mixture, in molecular proportions, of sodium and potassium carbonates.

In assaying, fusion is conducted in crucibles of graphite, clay, or sand, heated in crucible furnaces. Hessian crucibles are the best. For some purposes they must be lined with charcoal. This is done by making a mixture of finely pulverized charcoal and molasses, or solution of gum arabic. The mixture should be pliable but not moist to the touch. The crucible is filled with the mixture, which is then pressed down with a spindle of brass or box-wood to the proper shape (*Fig.* 8, *Pl. IV*), or else, the charcoal is bored out to the proper form. The crucible is then dried in a warm place.

A crucible should never be filled more than three-quarters full; and, when a crucible is removed from the fire, it should be tapped on the floor to settle the metal, and it must be kept covered while cooling. It should never be broken until perfectly

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cold. To break a crucible, it is hit with a hammer near the centre of the side so as to break off the top at one blow; then the bottom is placed on an anvil and cracked through so as to get the button out whole.

Crucibles are handled by means of crucible-tongs (*Fig.* 9, *Pl. IV*).

**Scorification and Cupellation.** — Scorification is a combination of roasting and fusion, conducted in the same manner as roasting but at a higher temperature. It is effected in scorifiers, (*Fig.* 10, *Pl. IV*) dishes made of a mixture of sand and clay. Scorifiers are broken in order to obtain the button resulting from the fusion, by placing them bottom up on an anvil, encircling with the left hand, and striking with a hammer. They are handled by means of scorifier-tongs (*Fig.* 11, *Pl. IV*).

Cupellation is also a combination of roasting and fusion, its object being to separate the lead from a button containing lead, silver, and gold. It is conducted in cupels, (*Fig.* 12, *Pl. IV*) made of bone-ashes, in the muffle of an assay furnace. Part of the lead oxidises and volatilizes as oxide, the remainder sinks into the cupel, leaving a bead of silver and gold. Cupels are handled by means of cupel-tongs (*Fig.* 13, *Pl. IV*).

**The Blowpipe.** — The blowpipe is of great use in the preliminary examination of substances. The best form, Plattner's (*Fig.* 14, *Pl. IV*), consists of a tube with a trumpet-shaped mouth-piece C, a cylinder for collecting moisture A, and a jet with a platinum tip *b*. The diameter of the orifice of the platinum tip is 0.4 or 0.5 millimeters. The blowpipe is held as represented (*Fig.* 15, *Pl. IV*), the elbows resting on a table. In using the blowpipe the mouth-piece is pressed against the slightly opened lips, and, by breathing through the nose, the cheeks are filled with air, which is forced into the blowpipe by the muscles of the cheeks; the palate closes the communication between the mouth and the lungs, breathing being continued through the nose. As the cheeks contract they are filled by expiration through the throat without interrupting the blowing.

The source of heat may be a candle, an alcohol lamp, or some lamp of special construction. The best form is Berzelius' (*Fig.* 16, *Pl. IV*), the burning material of which is rape-seed oil, a mixture of alcohol and turpentine, olive oil, etc. The wick must be kindled by directing, by means of a blowpipe, the flame of an alcohol lamp against it.

The blowpipe may be used for oxidising or reducing. The oxidising flame (*Fig.* 17, *Pl. IV*), is produced by inserting the blowpipe one-third of the width of the wick as represented. The oxidation takes place in front of *d*, the apex of the inner blue flame. This point *d* is the hottest part of the flame, and oxidation is induced

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by the presence of free oxygen in the air in front of *d* and the influence of this high temperature.

The reducing-flame (*Fig.* 18, *Pl. IV*), is produced by bringing the blowpipe over one end of the wick, but not inserting it in the flame. The reduction takes place between *d*, the apex of the cone of volatile matter, and *a*, the apex of the inner blue flame. In this space, the supply of oxygen being limited, the combustion is incomplete, and the highly heated particles of carbon, by their affinity for oxygen, have a powerful reducing action.

The following are the principal operations performed by means of the blowpipe in the preliminary examination of substances.

To determine the effects of simple heat a few small fragments of the substance are introduced into a matrass, or, if oxidation is feared, into a narrow test-tube, and a gentle heat is first applied by means of an alcohol lamp; then, the temperature is raised to ignition by means of the blowpipe. The common effects are decrepitation, fusion, or the elimination of volatile constituents.

To determine the effects of roasting, the substance is introduced into a glass tube open at both ends, 200 millimeters long and 6 millimeters in diameter; the tube is slightly inclined, the substance placed about 4 centimeters from the lower end, and heat applied to the tube immediately beneath the substance, by means of a lamp or blowpipe. The common effect is the production of volatile oxides.

To determine the effects of the oxidising and reducing flames, the substance is placed in a shallow cavity near one end of a piece of charcoal, and the flame of the blowpipe directed down upon it at an angle of about 20°, heating gradually at first with the oxidising, and then with the reducing flame. The common effects are the production of characteristic odors, volatilization, fusion, and the formation of coatings on the charcoal.

To determine fusibility and the coloration of the outer blowpipe flame, a small splintery fragment of the mineral is selected, and the pointed end is held, by means of a small platinum forceps, in the hottest part of the oxidising flame. The coloration by the reducing flame is also determined. Another method consists in pulverizing the mineral, moistening with water, and heating in the loop of a platinum wire. Metals, metallic sulphides, and oxides, are heated on charcoal.

To determine the effects of fusion with the fluxes (soda, borax, and salt of phosphorus) and, with cobalt nitrate solution, the substance must generally be freed from sulphur and arsenic, and the metals present must be oxidised. For this purpose the finely-pulverized substance is carefully roasted on charcoal in the oxidising flame, then heated in the reducing flame, and finally again in the oxidising flame;

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the assay is turned over and the operations are repeated; it is pulverized in an agate mortar, again placed on charcoal and the roasting completed.

*Borax.* — Fusion with borax may take place on platinum wire or on charcoal; for the former, the platinum wire is heated to ignition, dipped quickly into the borax, and the borax, taken up by the wire, is fused to a head in the oxidising flame; the dipping is repeated until the bead is sufficiently large; it must be perfectly transparent and colorless. The hot bead is then dipped into the pulverizad mineral and a small quantity is taken up; it is again fused, first in the oxidising flame, then in the reducing flame, and the color in each case is noted.

*Salt of Phosphorus.* — The bead is prepared as in the case of borax. This flux is useful in detecting silicates, the silica usually separating in the form of a skeleton floating in the fused mass.

*Soda.* — Certain substances combine with soda at a high temperature and form fusible or infusible compounds. The fusible compounds are those of silica and several metallic acid oxides. Fusibility in presence of soda is determined by mixing the soda and pulverized mineral on the palm of the left hand, and then pressing the moistened mixture into a shallow cavity in a piece of charcoal, and heating gently at first, to drive off water, and finally to ignition. In case the assay contains sulphur the bead is yellowish, and when placed on silver and moistened it communicates a dark stain.

Many oxides are reduced on charcoal alone; but, when in combination, oxides generally require the presence of a strong base to decompose the salts and liberate the basic oxides. Soda acts in this way, and being partially decomposed under the action of the blowpipe it furnishes volatilized sodium and oxygen, and the latter forms carbon monoxide with the charcoal — thus, two strong reducing agents are produced, sodium and carbon monoxide, which act upon the metallic oxides.

*Cobalt Nitrate Solution.* — Solution of cobalt nitrate is used to detect alumina, magnesia, zinc oxide and stannic oxide. The test is applied by pulverizing the mineral, rubbing up with water, placing it on charcoal and drying; a drop of the dilute solution is added and the assay is heated to a low red heat in the oxidising flame. The color is observed after cooling and always by day light.

The blowpipe tests are usually supplemented by the application of the wet process. The substance is dissolved in hydrochloric acid, either in the cold or by the assistance of heat. Effervescence indicates carbonic acid, or it indicates one of the higher oxides of a metal in which case chlorine will be given off. The solution is diluted and tested for the various bases and acids. Hydrochloric acid decomposes many silicates, the silica separating either in the gelatinous or in the pulverulent form.



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# REACTIONS OF THE PRINCIPAL BASES BEFORE THE BLOWPIPE.

| Bases. | Reaction on Charcoal in Platinum Forceps. | Reaction with Borax on Platinum Wire. | Reaction with Salt of Phosphorus on Platinum Wire. | Reaction with Soda. | Reaction with Cobalt Solution. |
|---|---|---|---|---|---|
| Potassa. | Violet outer flame. Alkaline. | | | | |
| Soda. | Yellow outer flame Alkaline. | | | | |
| Ammonia. | Pale green outer flame. Alkaline. | | | | |
| Silver Oxide. | Easily reduced to Silver | O. F. Partly reduced, partly absorbed, yielding milk-white bead. R. F. On charcoal grey or colorless bead. | O. F. Yellow bead. R. F. As with borax. | Reduced and fused instantly, the soda passing into the charcoal. | |
| Lime. | Unaltered. Carbonate becomes Alkaline. Pale red outer flame. | Easily fusible to clear glass. Carbonate fuses with effervescence to opaque and crystalline glass. | Fusible to clear glass. Excess gives milk-white glass. | Infusible on charcoal. Soda passes into charcoal. | |
| Magnesia. | Unaltered. Carbonate becomes Alkaline. | Same as lime. | Same as lime. | Same as lime. | Pink Color |
| Zinc Oxide. | O. F. Infusible. Yellow, while hot. R. F. Reduced and volatilized, yielding coating yellow, while hot, white when cold. | O. F. Easily fusible to bead, yellow while hot, white when cold. R. F. Reduced on charcoal, the metal volatilizes coating the charcoal. | Same as with borax. | O. F. No action. R. F. As with borax. At high temperature green flame. | Yellowish-green Color. |
| Cupric Oxide. | O. F. Fuses to black globule. R. E. Reduced and fused. | O. F. Hot, green lead; cold, blue. Colors flame green. R. F. Cold, red bead. | Same as with borax. | O. F. Hot, green bead; cold, colorless and opaque. R. F. On charcoal reduced easily to copper. | |
| Mercuric Oxide. | Instantly reduced and volatilized. | ..... | ..... | In matrass, sublimate of metallic mercury. | |



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| | | | | | |
|---|---|---|---|---|---|
| Lead Oxide. | On platinum foil fusible. On charcoal reduced to lead with effervescence. Charcoal coated yellow. | O. F. Fusible to yellow glass. R. F. On charcoal, reduced to colorless glass. | O. F. As with borax. R. F. On charcoal, gray. | O. F. On platinum wire easily fusible to yellow glass. R. F. On charcoal reduced to lead. | |
| Ferric Oxide. | O. F. Unaltered. R. F. Black and magnetic. | O. F. Hot, red bead; cold, yellow. R. F. Green bead. | O. F. As with borax. R. F. Hot, red bead; cold, brown. With tin, on charcoal green bead while cooling; cold, colorless. | O. F. Infusible. R. F. On charcoal reduced, leaving gray magnetic powder. | |
| Manganic Oxide | Infusible. The oxide and superoxide turn red ($Mn_3O_4$.) | O. F. Amethyst bead. R. F. Colorless bead. | O. F. Brownish-violet bead. Nitre brings out the color. R. F. Colorless bead. | O. F. On platinum wire a green bead, transparent while hot. R. F. Soda passes into charcoal. | |
| Alumina. | Unaltered. | Slowly fusible to clear glass. | As with borax. | On charcoal swells a little leaving infusible compound. | Blue Color. |
| Arsenious Oxide | Volatilized. | ..... | ..... | Reduced, gives off garlic odor. | |
| Tin Oxides. | O. F. Stannous oxide burns. Stannic oxide, yellow while hot. R. F. Reduced to metal. Yielding also coating of oxide. | O. F. Very slowly and in small quantity fusible to clear bead. | As with borax. | O. F. On platinum wire, with effervescence, infusible mass. R. F. On charcoal reduced to tin. | Bluish-green Color. |
| Silica. | Unaltered. | Slowly fusible to clear glass. | In minute quantity fusible to clear glass. | Fusible with strong effervescence to clear glass. | Pale Blue Color. |



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**Specific Gravity.** — The specific gravity of a body is the ratio of its weight to the weight of an equal volume of some substance assumed as a standard. The standard for solids and liquids is pure water at 15.5° C. (in France, at 4° C.); for gases, pure dry air at 15.5° C. (in France, at 0° C.) The specific gravity of solids and liquids is usually determined at 15.5° C.; that of gases, at the temperature of the air, being afterwards calculated at 15.5°.

There are three principal methods for determining the specific gravity of solids and liquids, — by the hydrostatic balance, by the specific-gravity flask, and by the hydrometer.

*The Hydrostatic Balance.* — The use of this apparatus depends upon Archimedes' Law: *A solid body immersed in a liquid loses a part of its weight equal to the weight of the displaced liquid.* The substance is weighed accurately in air ( $W^a$ ). It is then attached by a slip-knot to a horse-hair, is suspended from the short pan of a balance, allowed to hang freely in a vessel of distilled water and weighed ( $W^w$ ). The first weight should be the weight *in vacuo*, but for practical purposes the weight in air gives sufficiently accurate results. The weight in air divided by the loss of weight in water gives the specific gravity, $\frac{W^a}{W^a - W^w}$.

If the solid is lighter than water, a piece of lead is attached to sink it, and the weight of the substance in air ( $W^a$ ), of the lead in water ( $L^w$ ) and of the system in water ( $S^w$ ), is determined. The weight of the substance in air, divided by this weight minus the difference in the weight of the system and the lead in water, gives the specific gravity, $\frac{W^a}{W^a - (S^w - L^w)}$.

If the substance is soluble in water its loss of weight in some liquid in which it is insoluble is determined, as turpentine, benzene, etc. This is the weight of an equal bulk of the liquid, ( $W^a - W^l$ ). Then, as the specific gravity of the liquid (G) is to the specific gravity of water (1), so is the weight of a bulk of the liquid equal to that of the substance, to the weight of an equal bulk of water. The weight in air of the substance divided by the latter weight is the specific gravity.

$$G : 1 :: W^a - W^l : W^w . \frac{W^a}{W^w} .$$

The specific gravity of a liquid may also be determined by means of this apparatus, by weighing some substance in air ( $W^a$ ), in water ( $W^w$ ), and in the liquid ( $W^l$ ). The loss of weight in the liquid divided by the loss of weight in water gives the specific gravity of the liquid. $\frac{W^l - W^a}{W^w - W^a}$.

*The Specific-Gravity Flask.* — This apparatus is a tared flask holding to a mark on the neck a determinate weight of distilled water at 15.5° C. To determine the

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specific gravity of a solid, the latter is crushed and weighed in air, the flask is filled with distilled water to the mark, the substance dropped in, and the water again adjusted to the mark and the flask weighed. The weight of the flask after the substance has been introduced ( $F^s$ ) is subtracted from the sum of the weights of the substance ( $W^s$ ) and of the flask of water ( $F^w$ ). The weight of the substance divided by the weight thus obtained is the specific gravity. $\frac{W^s}{(W^s + F^w - F^s}$.

If the solid is soluble in water, some liquid, like benzene or turpentine, in which it is insoluble, is substituted, and the process conducted as before. The number obtained is the weight of the liquid displaced. Now, the specific gravity of the liquid (G) is to the weight of the liquid displaced ( $W^s - W^l$ ) as the specific gravity of water is to the weight of a bulk of water equal to that of the liquid displaced ( $W^w$ ), i. e., equal to that of the substance. The weight of the substance in air divided by the latter weight gives the specific gravity.

$$G : 1 :: W^s - W^l : W^w . \qquad \frac{W^s}{W^w} .$$

To determine the specific gravity of a liquid, the latter is brought to the required temperature, poured into the flask up to the mark, and the whole weighed. This weight ( $W^l$ ), minus the weight of the flask (F), divided by the weight of water required to fill the flask (W), gives the specific gravity of the liquid. The 100 c. c. flask is the most convenient size for this purpose. $\frac{W^l - F}{W}$.

*The Hydrometer.* — This instrument consists of a closed tube, expanded below into a bulb, the lower part of which is loaded to maintain the instrument in an upright position when floating. Its action depends upon the principle that a floating body displaces its own weight of liquid. The liquid to be tried is put in a narrow jar, and the instrument floated in it; when the hydrometer comes to rest the mark on the stem at the liquid-level is read off.

Hydrometers may be graduated to read specific gravities directly, or they may be graduated arbitrarily, as is the case with the Beaumé hydrometers. There are two kinds of Beaumé hydrometers, one for liquids heavier than water, and the other for liquids lighter than water.

The former was originally graduated by marking the point to which it sinks in pure water 0°, and the point to which it sinks in a solution of 15 parts common salt in 85 parts water 15°, dividing the interval into fifteen equal parts and continuing divisions of the same size beyond 15° to the bulb. This method is no longer used, the 0° is determined by water at 15° C. and the other fixed point is determined by means of pure sulphuric acid (Sp. Gr. 1.2427) at 15° C and is marked 66°.

The hydrometer for liquids lighter than water is graduated by marking the point



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to which it sinks in pure water 10°, and the point to which it sinks in a solution of 10 parts common salt in 90 parts water 0°, dividing the interval into ten equal parts and continuing divisions of the same size along the rest of the scale.

The degrees Beaumé can be readily converted into specific gravities. As the old method for graduating hydrometers for liquids heavier than water is no longer used, the old tables, constructed by means of the equation of Francoeur, and depending upon this method of graduation, are no longer of any use.

To convert degrees Beaumé into specific gravities, we now use, for liquids heavier than water, the formula

$$P = \frac{144.3}{144.3 - d},$$

and for liquids lighter than water,

$$P = \frac{146}{136 + d}.$$

In which P = specific gravity, and d = degrees Beaumé.

## HYDROMETER TABLES.

### For Liquids Heavier than Water.

| Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. |
|---|---|---|---|---|---|---|---|
| 0 | 1.0000 | 19 | 1.1516 | 38 | 1.3574 | 57 | 1.6527 |
| 1 | 1.0069 | 20 | 1.1608 | 39 | 1.3703 | 58 | 1.6719 |
| 2 | 1.0140 | 21 | 1.1702 | 40 | 1.3834 | 59 | 1.6915 |
| 3 | 1.0212 | 22 | 1.1798 | 41 | 1.3968 | 60 | 1.7115 |
| 4 | 1.0285 | 23 | 1.1895 | 42 | 1.4104 | 61 | 1.7321 |
| 5 | 1.0358 | 24 | 1.1994 | 43 | 1.4244 | 62 | 1.7531 |
| 6 | 1.0433 | 25 | 1.2095 | 44 | 1.4386 | 63 | 1.7748 |
| 7 | 1.0509 | 26 | 1.2197 | 45 | 1.4530 | 64 | 1.7968 |
| 8 | 1.0586 | 27 | 1.2301 | 46 | 1.4678 | 65 | 1.8194 |
| 9 | 1.0665 | 28 | 1.2407 | 47 | 1.4829 | 66 | 1.8427 |
| 10 | 1.0744 | 29 | 1.2514 | 48 | 1.4983 | 67 | 1.8665 |
| 11 | 1.0825 | 30 | 1.2624 | 49 | 1.5140 | 68 | 1.8909 |
| 12 | 1.0906 | 31 | 1.2735 | 50 | 1.5301 | 69 | 1.9161 |
| 13 | 1.0989 | 32 | 1.2849 | 51 | 1.5465 | 70 | 1.9418 |
| 14 | 1.1074 | 33 | 1.2964 | 52 | 1.5632 | 71 | 1.9683 |
| 15 | 1.1159 | 34 | 1.3081 | 53 | 1.5802 | 72 | 1.9955 |
| 16 | 1.1246 | 35 | 1.3201 | 54 | 1.5978 | 73 | 2.0235 |
| 17 | 1.1335 | 36 | 1.3323 | 55 | 1.6157 | 74 | 2.0523 |
| 18 | 1.1424 | 37 | 1.3447 | 56 | 1.6340 | 75 | 2.0819 |

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## For Liquids Lighter than Water.

| Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. | Deg. B. | Sp. Gr. |
|---|---|---|---|---|---|---|---|
| 10 | 1.000 | 23 | .918 | 36 | .849 | 49 | .789 |
| 11 | .993 | 24 | .913 | 37 | .844 | 50 | .785 |
| 12 | .986 | 25 | .907 | 38 | .839 | 51 | .781 |
| 13 | .980 | 26 | .901 | 39 | .834 | 52 | .777 |
| 14 | .973 | 27 | .896 | 40 | .830 | 53 | .773 |
| 15 | .967 | 28 | .890 | 41 | .825 | 54 | .768 |
| 16 | .960 | 29 | .885 | 42 | .820 | 55 | .764 |
| 17 | .954 | 30 | .880 | 43 | .816 | 56 | .760 |
| 18 | .948 | 31 | .874 | 44 | .811 | 57 | .757 |
| 19 | .942 | 32 | .869 | 45 | .807 | 58 | .753 |
| 20 | .936 | 33 | .864 | 46 | .802 | 56 | .749 |
| 21 | .930 | 34 | .859 | 47 | .798 | 60 | .745 |
| 22 | .924 | 35 | .854 | 48 | .794 | | |

The specific gravity of gases is determined as follows:

A very thin glass globe, fitted with a brass cap to the under side of which is attached a delicate thermometer, and which is surmounted by an excellent stop-cock, is exhausted by means of an air-pump as completely as possible and weighed. It is then filled from the generator with the dried and purified gas under a little pressure. The stop-cock is then opened for an instant to allow the gas to attain the same pressure as that of the air, and the globe weighed. It is again exhausted, filled with pure dry air and weighed. The weight of the gas divided by the weight of the air gives the specific gravity, provided neither temperature nor pressure have altered during the experiment.

### *Reagents.*

Reactions, or tests, for determining the presence of substances, take place generally in dilute solutions; hence, great care must be taken not to add too great excess of the reagent. The reagents to be reliable must be pure, it is therefore necessary to examine them for impurities.

**General Properties of the Metals and their Salts.** - Potassium, sodium and ammonium are called the *alkaline metals*, and their oxides are called *alkalies*. Barium, calcium, and strontium, are called the *alkaline earth metals*, and their oxides are called *alkaline earths*. These two groups constitute the *light* metals, the rest are called the *heavy* metals. The metals of the platinum group, together with gold, silver and mercury, are called the *noble* metals.

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The salts of the alkaline metals are all more or less soluble; those of ammonium are either volatile or decomposed by heat.

The carbonates, in general, are all decomposed by heat except those of the alkaline metals, and all are insoluble in water except those of the alkaline metals; all are more or less soluble in water containing carbon dioxide, and all are decomposed by the less volatile acids with effervescence.

The nitrates are all soluble and decomposed by heat.

The sulphates are soluble, except those of barium, strontium, calcium, and lead. They are all insoluble in alcohol.

Deliquescent salts, soluble, of course, in water, are also generally soluble in alcohol. Potassium carbonate is a marked exception.

**Tests for the Principal Bases and Acids.** — To determine the presence of the various bases and acids in their compounds, in solution, certain simple tests are generally applicable. This is generally the case with the impurities in commercial products. In the case of more complex mixtures a course of qualitative analysis may be necessary.

*Potassium.* — Tartaric acid gives a white, crystalline precipitate, the formation of which is promoted by agitation and by the addition of alcohol. Platinic chloride, with a little hydrochloric acid, if necessary, gives a yellow precipitate, the formation of which is promoted by the addition of alcohol. In very dilute solutions 24 hours will be required for the formation of either precipitate.

*Sodium.* — A yellow color is imparted to the outer flame of the blowpipe. Great care must be taken in the application of this test, on account of the almost universal presence of sodium.

*Ammonium.* — When heated with caustic soda or lime, ammonia is given off which is recognized by its peculiar odor, its alkaline reaction to test-paper, and by the white fumes produced with hydrochloric acid.

*Silver.* — Hydrochloric acid produces a white, curdy precipitate, turning black by exposure to light, which is insoluble in nitric acid, but soluble in ammonia.

*Calcium.* — Oxalic acid produces a white precipitate, insoluble in acetic acid.

*Magnesium.* — The soluble phosphates, with a little ammonia, produce a white crystalline precipitate, the formation of which is generally promoted by rubbing the sides of the vessel with a glass rod.

*Zinc.* — Sulphydric acid, and hydro-ammonium sulphide, with excess of sodium hydrate, produce a white precipitate.

*Copper.* — Ammonia in small quantity, precipitates the green hydrate, but excess of the reagent redissolves it, yielding a purplish-blue solution. Sulphydric acid, and hydro-ammonium sulphide, yield a black precipitate, insoluble in excess of the reagent.

*Alumimium* — Ammonia produces a white gelatinous precipitate insoluble in excess of reagent.

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*Antimony.* — Sulphydric acid yields an orange-colored precipitate, soluble in ammonium sulphide, reprecipitable by acids. With sulphuric acid and zinc in a Marsh apparatus, a dark metallic spot is deposited on a cold plate held in the flame of the escaping gases, which is insoluble in sodium hyposulphite.

*Arsenic.* — Sulphydric acid, with a little hydrochloric acid, produces a bright yellow precipitate, soluble in ammonia, reprecipitable by acids. With sulphuric acid and zinc in a Marsh apparatus, a dark metallic spot is deposited on a cold plate held in the flame of the escaping gases, which is soluble in sodium hyposulphite.

*Lead.* — Sulphuric acid produces a white precipitate which is insoluble in nitric acid. Sulphydric acid, and hydro-ammonium sulphide, produce a black precipitate. Potassium chromate produces a yellow precipitate.

*Tin.* — Mercuric chloride produces a grey or white precipitate in *stannous* salts.

*Iron.* — Potassium, sodium, and ammonium hydrate, produce white precipitates in *ferrous* salts, brown in *ferric* salts. Potassium ferro-cyanide yields Prussian blue with *ferric* salts, potassium ferri-cyanide the same with *ferrous* salts.

*Manganese.* — Hydro-ammonium sulphide produces a flesh-colored precipitate.

*Chlorine.* — Silver nitrate gives with the soluble chlorides a white, curdy precipitate, turning black by exposure to light, which is insoluble in nitric acid, but soluble in ammonia.

*Nitric Acid.* — A layer of ferrous sulphate solution, poured carefully over a solution containing nitric acid or nitrates, the latter having been previously mixed with an equal volume of sulphuric acid and allowed to cool, is colored black or brown at the surface of contact of the two liquids.

*Sulphuric Acid.* — Barium chloride or nitrate produces, in solutions of sulphuric acid, or the soluble sulphates, a white precipitate insoluble in nitric acid.

*Sulphydric Acid.* — Lead acetate or silver nitrate produce a black precipitate.

*Carbon Bisulphide.* — The vapor is readily detected by the formation of a black precipitate in a solution prepared by boiling litharge in caustic potash solution. Sulphydric acid does not interfere with this test.

**Solvents.** — The great solvent is water, and next to this is alcohol, although glycerine is almost as extensively used to-day in that capacity.

*Distilled Water*, $H_2O$. — Pure water is obtained by distilling spring water in an ordinary still or in a glass retort; the first and last portions of the distillate are rejected. It should leave no residue when evaporated in a platinum vessel, should not effect litmus paper, and should give no precipitate with hydro-ammonium sulphide, ammonium nitrate, ammonium oxalate, silver nitrate, barium chloride, auric chloride or mercuric chloride, and sodium carbonate.

*Alcohol*, $C_2H_6O$. — The alcohol used in analysis, is either absolute alcohol or spirit of wine of various degrees of strength. Alcohol is principally prepared by fermenting sugar and concentrating the product by fractional distillation.

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**Acids.** — The three great commercial acids are sulphuric, nitric and hydrochloric.

*Sulphuric Acid*, $H_2SO_4$. — Commercial sulphuric acid is prepared by oxidising sulphurous oxide, obtained by combustion of sulphur, or roasting of native sulphides, by means of nitric acid. It is liable to contain lead, arsenic, and nitrogen compounds. Chemically pure sulphuric acid, concentrated and dilute, is required in analysis, and must be tested for the above impurities. It should leave no residue upon evaporation. To test for lead it is diluted, saturated with ammonia and sulphydric acid is added. The presence of lead will be indicated by a black precipitate.

Sulphuric acid, on account of its great affinity for bases, and because it volatilizes at a comparatively high temperature only, is used to decompose salts. It is also used to absorb water, for which it has a great affinity, and is a test to detect the presence of barium and lead, the sulphates of these metals being insoluble. In diluting this acid great heat is evolved, therefore the acid should always be poured into the water, never the reverse, as the steam generated at the surface of contact of the lighter water may expel the latter into the face of the operator.

*Nitric Acid*, $HNO_3$. — Commercial nitric acid is prepared by heating sodium or potassium nitrate with sulphuric acid, and condensing the product. Pure nitric acid for analysis should have a specific gravity of 1.2. It should leave no residue upon evaporation, and should be free from sulphuric and hydrochloric acids. Red fuming nitric acid contains hypo-nitric acid.

Nitric acid is used as a solvent, especially for the metals, and is also the great oxidising agent.

*Hydrochloric Acid*, H Cl. — The commercial acid is prepared by heating common salts with sulphuric acid and condensing the product. It is purified by diluting to sp. gr. 1.12, and distilling with addition of sodium chloride. Pure hydrochloric acid should have a specific gravity of 1.12, it should be colorless, leave no residue upon evaporation, and should contain no chlorine, sulphurous or sulphuric acid. Free chlorine is detected by means of a solution of potassium iodide and starch-paste, which produces a blue tint if chlorine is present. The liquid is made faintly blue with iodide of starch, if it is discolored, sulphurous acid is present.

Hydrochloric acid is used as a solvent, principally for metals, oxides, sulphides, and carbonates. It is also used as a test to detect the presence of silver and ammonia. It was formerly called muriatic acid.

*Nitro-Muriatic Acid* (*Aqua Regia*). — This is a mixture of 1 part pure nitric acid with 3 or 4 parts pure hydrochloric acid. It is a most powerful solvent for all metals except those whose chlorides are insoluble.

*Sulphydric Acid*, $H_2S$. — This is prepared by placing coarsely-powdered iron mono-sulphide in the flask, (*Fig* 1, *Pl. V*), and adding concentrated sulphuric acid by the funnel. The small bottle contains water by which the gas is washed. It is used either in the form of gas, or in solution in water. When sufficient gas has been evolved, the liquid is poured off the sulphide and the bottle rinsed. The

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solution in water rapidly oxidises; hence, it is always prepared fresh. Sulphydric acid is used principally as a test for the metals in solution, forming with them precipitates of characteristic colors.

*Oxalic Acid*, $C_2 H_2 O_4 . 2 H_2 O$. — The commercial acid is prepared mostly from sawdust, by fusion with alkalies. It is purified by re-crystallization. The pure acid should leave no residue when heated in a platinum dish. It is used as a test for calcium salts, and, in volumetric analysis, to standardize potassium permanganate.

*Silica*, $Si O_2$. — This is our cheapest acid oxide.

**Bases.** — The bases proper are metallic hydrates; but, as the metallic oxides, and even the metals, act in a similar manner under the circumstances in which reactions generally take place, they are here included.

*Potassium Hydrate*, K H O, *and Sodium Hydrate*, Na HO. — These bases are prepared by decomposing the carbonates in solution, by means of calcium hydrate; the hydrates remain in the solution, which is decanted from the precipitated calcium carbonate, concentrated by evaporation, and allowed to solidify in cooling.

They are the strongest bases, are very deliquescent, and have a great affinity for carbon dioxide, so that they must be kept in stoppered bottles. They are called the *fixed* alkalies. They are used on account of their affinity for acids, and because they are not volatilized except at a very high temperature, for decomposing salts and separating basic oxides: they are also strong solvents. When used in solution, the sp. gr. is usually 1.13 to 1.15, or 1 part of the base is dissolved in 5 parts water.

*Ammonia*, $N H_3$, *Aqua Ammoniæ*, $NH_4 . HO$. — The gas is prepared by heating ammonium chloride with moist calcium hydrate. When absorbed by water (which is capable of absorbing 700 times its volume) the solution constitutes *aqua ammoniæ*.

Solution of ammonia should be colorless, should leave no residue when evaporated, and should contain no sulphuric, hydrochloric, or carbonic acid, or metallic impurities. Carbonic acid, which it is liable to absorb from the air, is detected by the cloudiness produced by the addition of lime water. Before testing for the other impurities, it must be super-saturated with nitric acid. The solution must be kept in stoppered bottles, and, when used, the bottle should be held above the level of the eyes, to prevent the vapor from entering the eyes.

Ammonia is called the *volatile* alkali, it is a strong base, and is used to neutralize acids and to precipitate bases. The solution commonly employed in analysis has a specific gravity of 0.96.

*Lime*, Ca O, *Calcium Hydrate*, $Ca O_2 H_2$. — Lime is prepared by calcining limestone. Calcium hydrate is prepared by adding to pure calcined lime in a porcelain dish, half its weight of water: it is preserved in stoppered bottles. Lime water is prepared by digesting calcium hydrate with cold water; no filtration is necessary as the liquid settles clear.

Lime is our great base; it is not quite so strong as the alkalies, but is much

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cheaper. Besides its principal use, lime water is used to detect carbon dioxide, which causes the formation of a pellicle of calcium carbonate on the surface of the liquid when present in the atmosphere.

*Zinc*, Zn. — Commercial zinc (spelter) is prepared largely from the native sulphide. It is malleable between 120° and 150° C, and can be converted into sheets, or foil. Granulated zinc is prepared by dropping melted zinc into cold water.

Zinc for analytical purposes, is tested by dissolving in sulphuric acid in a flask with a gas-evolution tube, the outer limb of which is under water; lead and copper remain undissolved; when the action is complete the water is allowed to recede into the flask; after cooling, a dilute solution of potassium permanganate is added drop by drop, and, if a drop imparts the same red tint as to an equal volume of acidulated water, it is free from iron. Arsenic is detected by Marsh's apparatus; for analytical purposes not a trace of arsenic should be present.

Zinc is used for the preparation of hydrogen, to precipitate copper and to reduce ferric to ferrous salts.

*Litharge*, Pb O. — Litharge is prepared by heating the metal with access of air. It should be dry and free from red oxide. It should be assayed for silver, by fusing in a crucible

| | | |
|---|---|---|
| Litharge | 120 | grammes. |
| Soda | 60 | " |
| Charcoal | 0.7 | " |

covered with a layer of dried salt, one-quarter of an inch thick. The crucible is allowed to cool, and the lead button obtained is placed, in a bone-ash cupel, in the muffle of an assay furnace, and heated until all the lead is oxidised. The bead of silver remaining is weighed. Litharge is largely used in assaying. It acts as an oxidising and desulphurizing agent and as a basic flux.

**Salts.** — *Ammonium Carbonate*, $(NH_4)_2\,CO_3$. — This salt is prepared by heating ammonium chloride with calcium carbonate and condensing the volatile product. The commercial salt is prepared by the dry distillation of bones, horns, etc.

When pure it should volatilize completely, and after super-saturation with nitric acid, it should not produce a precipitate with barium nitrate, silver nitrate, or sulphydric acid. It is used to precipitate the bases whose carbonates are insoluble. The solution used in analysis contains 1 part of the salt to 4 parts water.

*Ammonium Chloride*, $NH_4$ . Cl. — Prepared from the ammoniacal liquid of the gas works, by converting all ammonia salts into chlorides by the addition of hydrochloric acid, evaporating to dryness, heating to expel tarry matter, and purifying by sublimation.

The pure salt should leave no residue on evaporation, should be neutral to test paper, and produce no precipitate with ammonium hydro-sulphide. It is used in analysis to retain certain salts in solution by forming double compounds with them. The solution contains 1 part of the salt to 8 parts water.

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*Ammonium Oxalate*, $C_2 (NH_4)_2 O_4 . 2 H_2 O$. — Prepared by neutralizing a hot solution of oxalic acid with ammonia, or ammonium oxalate. It is used to detect and estimate lime, with which it forms insoluble calcium oxalate. The solution containe 5 parts of the salt in 100 parts water.

*Ammonium Hydro-Sulphide*, $NH_4 . HS$. — Obtained by saturating a solution of ammonia with sulphydric acid. The solution must be kept in stoppered bottles as it is liable to oxidation.

It should leave no residue when evaporated at a red heat, and should not be rendered turbid by solutions of magnesia or lime. It is one of the most frequently used reagents in the laboratory, principally, as a test for the metals, with which it forms characteristic precipitates.

*Acid Sodium Borate*, (*Borax*), $2 Na BO_2 . B_2 O_3 . 10 H_2 O$. — This salt is found native in the waters of lakes in Thibet and Persia, and is manufactured from the native boric acid of Tuscany and the calcium borate of Peru. For use, it is fused and pulverized. It should give no precipitate with solutions of sodium carbonate, nor, after addition of nitric acid, with barium nitrate or silver nitrate. It is used, on account of its affinity for bases, in analysis by the dry method.

*Sodium Carbonate*, $Na_2 CO_3 . 10 H_2 O$. — This most important compound is now prepared principally from common salt, first converting into sulphate by heating with sulphuric acid, then reducing the sulphate to sulphide by calcination with coal-dust, and finally converting the sulphide into carbonate by calcination with calcium carbonate. It is purified by crystallization.

The pure salt should be white, leave no residue when dissolved in water, and its solution, after super-saturation with nitric acid, should not give a precipitate with barium chloride or silver nitrate. It is used in analysis in crystals and in solution, the latter containing 1 part of anhydrous salt in 5 parts water. It is used to precipitate the metals whose carbonates are insoluble, to neutralize acids and to decompose infusible compounds and form fusible ones. When used for assaying it should be dry and free from lumps. It acts as a desulphurizing and oxidising agent and as a basic flux.

*Sodium "Hyposulphite,"* $Na_2 S_2 O_3$. — properly called Thiosulphate.—This salt is prepared from the sulphite by addition of sulphur. It is used to precipitate certain metals, and as a solvent for certain salts : it is employed in volumetric analysis.

*Mixed Potassium and Sodium Carbonates.* — Prepared by igniting pure sodio-potassic tartrate, leaching with water and evaporating the solution to dryness. Used principally to decompose insoluble silicates and sulphates, instead of the separate carbonates, as it requires less heat for fusion.

*Potassium Cyanide*, K C N. — Prepared by heating potassium ferro-cyanide with potassium carbonate (Liebig), and by several other processes. It is a powerful



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reducing agent in the dry way and is extensively used to reduce compounds of the metals in assaying. It is pulverized in a mortar covered carefully with a towel as the dust is very poisonous. For use in solution 1 part is dissolved in 4 parts water, and it is kept in stoppered bottles. It forms precipitates with metallic salts and is used to separate metals in solution.

*Potassium Ferrocyanide*, $K_4$ Fe $C_6$ $N_6$ . 3 $H_2$ O. — This salt is used extensively in analysis, as it forms precipitates with most metallic salts, which exhibit characteristic colors. The solution contains 1 part of the salt to 12 parts water. In acidified solutions it gives colored precipitates, thus: —

| | |
|---|---|
| Antimony, white. | Copper, brown. |
| Cobalt, yellowish-green. | Iron, deep blue. |

*Potassium Nitrate*, K N $O_3$. — Nitre is largely used as an oxidising agent. When used in assaying it is finely powdered, dried and assayed for its oxidising power. A crucible is charged with

| | |
|---|---|
| Nitre, | 3 grammes. |
| Charcoal, | 1 " |
| Litharge, | 40 " |
| Soda, | 20 " |

covered with a layer of salt ½ inch thick, fused in a hot fire, removed, cooled and the button weighed. The difference between the weight of the button obtained and that given in the assay of the charcoal, divided by three, gives the oxidising power of nitre per gramme.

*Argol* — crude acid potassium tartrate. — Acts as a basic flux and reducing agent. It is pulverized, dried, and its reducing power determined. For this purpose a crucible is charged with

| | |
|---|---|
| Argol, | 2 grammes. |
| Litharge, | 20 " |
| Soda, | 10 " |

covered with a layer of salt ½ inch thick, fused in a hot fire, allowed to cool, the button extracted and weighed. Dividing by two, gives the amount of lead one gramme will reduce from litharge.

*Silver Nitrate*, Ag $NO_3$. — Prepared by dissolving silver in nitric acid. For solution 1 part of the salt is dissolved in 20 parts water. It should be neutral to test paper, the solution left after precipitating all the silver by means of hydrochloric acid should leave no residue on evaporation, and should give no precipitate with sulphydric acid. It is used to detect and estimate chlorides.

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*Barium Chloride*, $Ba\,Cl_2 . 2\,H_2O$. — This salt is prepared by decomposing the carbonate by means of hydrochloric acid. Its solution should be neutral, and should not be affected by sulphydric acid or ammonium hydro-sulphide; when completely precipitated by excess of sulphuric acid, the solution remaining should leave no residue on evaporation. It is used principally for the detection and estimation of sulphuric acid. The solution for qualitative testing contains 1 part barium chloride and 10 parts water.

*Calcium Chloride*, $Ca\,Cl_2$. — Prepared by decomposing the carbonate with hydrochloric acid. Its solution should be neutral, and should not be affected by ammonium hydro-sulphide, and it should not evolve ammonia when mixed with potassium hydrate. The solution contains 1 part of the salt in 5 parts water. It is used for the separation of organic acids. The salt is very deliquescent, and is therefore used in the solid state, after previous fusion, to absorb moisture.

*Ferric Chloride*, $Fe_2\,Cl_6$. — Prepared by acting upon iron with dilute hydrochloric acid and passing chlorine through the solution. It should not contain excess of acid, the presence of which is determined by the non-formation of a precipitate when a drop of ammonia is added, and it should not be colored blue by potassium ferricyanide. It is used to separate organic acids into groups, to detect certain organic acids and to decompose phosphates of the alkaline earths.

*Ferrous Sulphate*, $Fe\,SO_4 . 7\,H_2O$. — Prepared by the action of sulphuric acid on iron, or by oxidation of iron pyrites. The solution should give no precipitate with sulphydric acid after addition of hydrochloric acid. It is a powerful reducing agent, absorbs oxygen readily from the air, and is converted into ferric sulphate. It is used to detect nitric acid and to precipitate gold.

*Stannous Chloride*, $Sn\,Cl_2$. — Prepared by boiling powdered tin in hydrochloric acid. It should not be rendered turbid by sulphydric acid. It is a powerful reducing agent, and is used to withdraw chlorine from chlorides.

**Miscellaneous.** — *Charcoal* acts as a reducing agent and desulphurizer. It should be finely pulverized, and when used for assaying its reducing power is determined. A crucible is charged with

| | |
|---|---|
| Charcoal, | 1 gramme. |
| Litharge, | 40 " |

covered with a layer of salt ½ inch thick and fused; the weight of the button gives the amount of lead one gramme will reduce from litharge.

*Black Flux* is prepared by deflagrating 1 part nitre and 2 parts argol.

*Black Flux Substitute* is a mixture of 3 parts flour and 10 parts acid sodium carbonate. Both act as reducing agents.

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*Litmus* is prepared in Holland from a species of lichen; the ground lichens are treated with urine and potash and allowed to ferment, producing a purple-red, the true color of litmus, this is then treated with lime and more urine and again fermented, producing the blue commercial article. The lime, and the ammonia produced in the fermentation of the urine, being alkaline, alter the original red color to blue.

*Blue litmus papers* are prepared by dipping unsized paper in infusion of litmus. When such paper is immersed in an acid the latter neutralizes the alkali, thus restoring the original red color; hence, its use in detecting free acid.

*Red litmus paper* is prepared by dipping unsized paper in solution of litmus which has been turned red with sulphuric acid. It is used to detect alkalies, which turn it blue.

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# PART II.

# SPECIAL ANALYSES.

## SECTION 1.

### Gunpowder.

Gunpowder is a mechanical mixture of nitre, charcoal and sulphur. For military purposes the proportions of the ingredients used are

Nitre, 75; Charcoal, 15; Sulphur, 10.

Its composition does not differ much for that expressed by the formula

$$2\,K\,N\,O_3 + 3\,C + S,$$

which corresponds to the composition

Nitre, 74.833; Charcoal, 13.324; Sulphur, 11.843.

Composition of Gun Powder by Analysis. — Waltham Abbey Pebble Powder.

| | | | |
|---|---|---|---|
| Nitre, | | | 74.67 |
| Charcoal, viz. | Carbon | 12.12 | 14.22 |
| | Hydrogen, | 0.42 | |
| | Oxygen, | 1.45 | |
| | Ash, | 0.23 | |
| Sulphur, | | | 10.07 |
| Water, | | | 0.95 |
| Potassium Sulphate, | | | 0.09 |
| | | | 100.00 |

The ingredients of gunpowder do not act upon each other at ordinary temperatures, neither does the mixture explode readily by concussion, but when heated to a temperature of 315° C. or over, the elements arrange themselves in new forms. The principal chemical change which takes place, is the oxidation of the carbon at the expense of the oxygen of the nitre, and the explosive effect is largely due to this



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action, which not only produces a gas from solid material, involving a great change of volume, but also produces great heat which expands the gas thus produced.

In ordinary combustion the oxygen required is obtained from the air. It is possible, however, to have combustion without air; for there are several substances, containing a large amount of oxygen, and in which the oxygen-atoms are held in combination by such a feeble force that they give it up readily, which will furnish oxygen to a combustible as readily as the atmosphere and in a vastly more concentrated form. Nitre is such a substance, one gramme of this salt contains 350 c. c. of oxygen, measured at 15° C. There are several other substances which contain considerable oxygen and give it up readily, but they either explode by percussion when mixed with combustibles (potassium chlorate), or absorb moisture from the atmosphere (sodium nitrate).

Sulphur is used to give density and solidity to the grain, but its chief value arises from its great inflammability, thus facilitating ignition, and by its oxidation it increases the temperature, thus promoting combustion. It combines also with potassium, thus preventing the latter from combining with carbon dioxide which would diminish the gaseous products.

**Explosion.** — Assuming the following simple expression for the explosion of gunpowder, the volume of gas produced by a given amount of gunpowder can be calculated.

$$2\,K\,N\,O_3 + 3\,C + S = SK_2 + 3\,CO_2 + 2\,N.$$

*Problem.* — Required the volume of gas evolved in the explosion of one cubic centimeter of gunpowder, the gas being measured at the temperature produced by the explosion, 2200° C.

*Solution.* — The *apparent* specific gravity of gunpowder, that is, the weight of a given volume, including interstices, as compared with an equal volume of water, is about 0.9 or nearly unity; hence, 1 c. c. weighs about 1 gramme.

**1st Method.** —

$$\overbrace{2\,K\,N\,O_3 + 3\,C + S}^{270.2} = \overbrace{K_2\,S}^{\text{Solid}} + \overbrace{3\,CO_2 + 2\,N}^{\text{4 volumes Gas}}$$

By the principles of stochiometry, we have the proportion,

$\frac{270.2}{2} : 4 :: \frac{1}{.0896} : x = .330$ Litres $= 330$ c. c., measured at 0° C, or,

$273 : 273 + 2200 :: 330 : y = 2990$ c. c. Gas, measured at 2200° C.

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**2nd Method.** —

$$\overbrace{2\,K\,N\,O_3 + 3\,C + S}^{270.2} = \overbrace{K_2\,S}^{\text{Solid}} + \overbrace{3\,CO_2}^{132} + \overbrace{2\,N}^{28}$$

270.2 : 132 :: 1 : x = 0.488 grm. $CO_2$ produced.

270.2 : 28 :: 1 : y = 0.104 " N "

1 litre (1000 c. c.) Hydrogen, at 0° C, weighs 0.0896 grm.

Specific gravity of $CO_2 = \frac{44}{2} = 22$, of $N = \frac{28}{2} = 14$.

1000 c. c. of $CO_2$, at 0° C, weigh $22 \times 0.0896 = 1.97$ grm.

1000 c. c. of N, at 0° C, weigh $14 \times 0.0896 = 1.25$ grm.

1.97 : 1000 :: 0.488 : x′ = 247 c. c. $CO_2$.

1.25 : 1000 :: 0.104 : y′ = 83 c. c. N.

330 c. c. Gas at 0° C.

273 : 273 + 2200 :: 330 : z = 2990 c. c. Gas, measured at 2200° C.

Hence, in the explosion of gunpowder, the original volume is increased nearly three thousand times, which sufficiently accounts for the effects.

The products of explosion, as determined by analysis, are much more complex than is indicated by the above reaction. When one gramme of gunpowder is burnt, the solid products amount to about 0.57 gramme, and the gaseous products to about 0.43 gramme. The solid products are chiefly a mixture of potassium carbonate, sulphate, thio-sulphate, and sulphide, with remains of unburnt powder in very varying proportions. The composition of the gaseous products is more constant and does not differ much from 50 per cent. $CO_2$, 11 per cent. CO, 34 per cent. $N_2$, 3 per cent. $H_2S$ and 2 per cent. $H_2$. One gramme gunpowder furnishes 280 c. c. of gas, measured at 0° C.

**Nitre.** — Potassium nitrate, $K\,N\,O_3$, nitre or saltpetre, is a natural product, appearing as an efflorescence on or near the surface of the soil in dry climates, especially in India. It is produced there by the oxidation of ammonia, derived from decomposing organic matter, in the presence of some strong base, as potash, derived from decomposing rock-material.

This natural process is imitated in France, Germany and Russia, in the *nitre-beds* — heaps of decomposing organic matter, to which lime is added as a base, thus facilitating the oxidation of the ammonia and producing principally calcium nitrate. This is leached from the mass and decomposed by means of potassium carbonate:

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calcium carbonate is insoluble and is therefore precipitated, potassium nitrate remains in solution and is crystallized out.

Gunpowder for military purposes is still made of the nitre obtained from India, in England and the United States, or from the nitre-beds in France, Germany, and Russia. But a large supply of nitre for other powders is now made by decomposing the sodium nitrate found in extensive beds in Peru and Chili, by means of potassium chloride. The sodium nitrate is dissolved and the solution boiled, potassium chloride is then added by degrees, the sodium chloride precipitated is removed with a perforated ladle as fast as it is deposited; the liquid, after depositing suspended impurities, is run into the crystallizing pans. The principle upon which the reaction depends is the first law of Berthollet, sodium chloride being much less soluble in boiling water than either of the reagents used. The potassium chloride used is imported in large quantities from the salt mines of Stassfurt, Saxony; where it occurs as carnellite, $K\,Cl\,.\,Mg\,Cl_2\,.\,6\,H_2\,O$, an immense saline deposit underlying the rock salt. Potassium carbonate is also used in place of the chloride; it is now largely made from the native carnellite of the Stassfurt beds, just as sodium carbonate is made from common salt, it is also obtained from the residue of the stills in the manufacture of beet-root sugar, the third and newer process is from the "suint," or residue from the wash-water of wool-factories, the potassium salts having been deposited from the perspiration and accumulated on the thick wood. The crude potassium carbonate from wood-ashes, which formerly represented nearly the whole of the world's product, now furnishes not over forty per cent. of the general stock in market.

Crude nitre, in the form in which it is imported, contains a quantity of extraneous matter varying from 1 to 10 per cent. The principal impurities are moisture, sand, and organic matter, potassium and sodium chlorides, potassium, sodium, and calcium sulphates, and in that prepared from sodium nitrate a little of the latter generally remains. It is purified or refined by solution and re-crystallization. Its crystalline form is a six-sided prism, terminated by dihedral summits. Its specific gravity is 2.07.

The impurities in crude nitre are estimated as follows.

*Moisture.* — The moisture is determined by heating 50 grm. in a platinum crucible to a temperature not beyond the melting point, and determining the loss of weight. If calcium or magnesium nitrates are present, 1 grm. of dry potassium chromate is added to prevent their decomposition,

*Insoluble Matter.* — The fused mass is treated with water, filtered and the insoluble matter dried and weighed.

*Chlorides.* — The filtrate is contentrated by evaporation to a volume N. Reserve one-third of this solution for the estimation of the chlorides, another for that of the sulphates and a third for that of the calcium salts. Say it measures 150 c. c.

Fifty c. c. are placed in a clean porcelain dish, about 30 milligrammes of pure

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potassium chromate are added, and the solution is stirred until the salt is dissolved, coloring the solution distinctly yellow. A centinormal solution of silver nitrate is prepared by dissolving 1.7 grm. in 1 litre water, 1 c. c. = .00585 Na Cl. This solution is carefully added from a burette or pipette, graduated to $\frac{1}{10}$ c. c., the solution being constantly stirred, until the red color just begins to be permanent. The amount of silver nitrate solution required is noted. If either the solution of nitre or the silver solution be acid, it must first be neutralized with caustic potash. Suppose 2.6 c. c. of the centinormal silver solution be required, then $2.6 \times 3 \times 2 \times .00585 = 0.09$, the percentage of Na Cl in the nitre.

*Sulphates.* — The sulphates are estimated by means of a centinormal solution of barium chloride, prepared by dissolving 2.44 grammes of the crystallized salt. $Ba\ Cl_2 . 2\ H_2\ O$, in 1 litre water, 1 c. c. = .00142 gramme $Na_2\ SO_4$ or to .00174 gramme $K_2\ SO_4$.

Fifty c. c. of the solution N are placed in a platinum dish, mixed with a few drops of acid, then heated to boiling and the centinormal barium chloride solution added from a burette. The number of c. c. required to precipitate the sulphates is noted. The end of the reaction is determined as explained in the analysis of gunpowder for sulphur. Say 6.5 c. c. are required, then $6.5 \times 3 \times 2 \times .00174 = 0.07$ per cent. $K_2\ SO_4$ in the nitre.

*Calcium Salts.* — The calcium salts are estimated by means of a centinormal solution of ammonium oxalate, prepared by dissolving 160 grammes of the crystallized salt, $C_2\ (NH_4)_2\ O_4 . 2\ H_2\ O$, in 1 litre of water, 1 c. c. = .00102 gramme calcium nitrate. The number of c. c. required to precipitate the calcium salts is noted. The end of the reaction is determined as in the estimation of the sulphates Say 10 c. c. are required, then $10 \times 3 \times 2 \times .00102 = 0.06$ per cent. calcium nitrate in the nitre.

*Valuation of Nitre.* — To determine the amount of pure potassium nitrate in a sample of the crude salt, the following method of Abel and Bloxam, of the Woolwich Arsenal, is recommended as the best method now known.

1.5 gramme of the sample is well mixed in a platinum crucible with 2 grammes finely-powdered resin, or better with 0.4 gramme of Brodie's finely-divided graphite. and 5.3 grammes pure dry common salt. The heat of a wire-gauge flame is applied until no more vapor is given off; the crucible is allowed to cool down a little, and 1.7 gramme potassium chlorate are added; gentle heat is applied until most of the chlorate is decomposed, then it is heated to bright redness for three minutes. The mass should be liquid and free from floating charcoal. When cool it is removed to a funnel and the crucible washed with boiling water. The mass is then dissolved in hot water. and the solution, colored with litmus, is neutralized by means of a normal solution of sulphuric acid added from a burette.

Brodie's carbon is prepared by mixing coarsely-powdered graphite with $\frac{1}{4}$ its weight of potassium chlorate, the mixture is added to a quantity of strong sulphuric

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acid equal to twice the weight of the graphite and heated in a water bath until yellow vapors cease to be evolved. The mass is allowed to cool, is washed, dried and ignited. It swells up and leaves finely-divided graphite.

The normal solution of sulphuric acid is prepared by mixing about 300 c. c. of pure sulphuric acid of specific gravity 1.84, or thereabouts, with three or four times its volume of distilled water, allowing to cool and then diluting to 1 litre. 53 grms. of pure dry sodium carbonate, $Na_2 CO_3$, are then dissolved and the solution diluted to 1 litre. 10 c. c. of this solution are placed in a small beaker with a few drops of litmus solution, and the sulphuric acid is added from a pipette graduated to $\frac{1}{10}$ c. c. until the point of neutrality is reached. Suppose 8.9 c. c. are required, then 890 c. c. of the acid solution made up to 1 litre wilt be of the required strength.

Refined saltpetre need only be tested for chlorides, the most injurious of the impurities, becanse they are generally deliquescent salts, thus rendering the powder liable to absorb moistnre. Generally the following is a sufficient test. A normal solution of silver nitrate is prepared, containing 170 grammes, to the litre. Ten grammes of the refined saltpetre are dissolved, and 1 c. c. of the standard silver nitrate solution is added. After standing for 24 hours it is filtered, and the liquid divided into two portions. To one silver nitrate is added, to the other solution of sodium chloride. One will produce a precipitate: if it is the silver salt, the nitre contains more than .00016 of its weight of sodium chloride; if it is the sodium chloride it contains less than this amount and is sufficiently pure for the manufacture of gunpowder. The solution of refined nitre should have no action on red or blue litmus paper.

**Sulphur.** — The principal source of the sulphur of commerce is the native sulphur of the mines of Sicily, where it occurs in calcareous formations of Miocene age, associated with gypsum and rock-salt. It is separated from the earthy matter by fusion, or, when the ore is poor, by distillation, and then constitutes *rough sulphur*, in which form it is exported. It contains about 3 per cent. of foreign matter.

Rough sulphur is usually purified by redistillation in an iron still, and condensation in a brick chamber in the solid state as *sublimed sulphur* (flowers of sulphur), which is afterwards melted and cast into moulds forming *roll sulphur*. But for the manufacture of gunpowder the sulphur is heated in an iron still and collected in the liquid form in a small receiver cooled by water, as *distilled sulphur*. Sublimed sulphur contains a large proportion of the variety insoluble in carbon bisulphide, or electro-positive sulphur, whereas distilled sulphur consists entirely of the soluble or electro-negative variety. The electro-positive does not act as well in gunpowder as the electro-negative, the reason seems to be that this variety is liable to contain sulphurous and sulphuric acid vapors, and also because the electrical state determines the chemical action of the elements.

The purity of crude sulphur is determined by heating and burning 20 grammes

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in a porcelain crucible and weighing the residue; or by dissolving 10 grammes in 50 c. c. carbon bisulphide, washing the residue with ether and weighing.

Refined sulphur contains small proportions of arsenic, antimony, iron and earthly matter. A qualitative test for their presence, together with a direct estimation of the sulphur, is sufficient. Refined sulphur should leave scarcely a trace of incombustible matter, when intended for use in the manufacture of gunpowder. After stirring it with warm water it should not redden litmus paper.

Ten grammes of the sulphur are burnt in a porcelain crucible; the residue contains the iron and earthy matters. The iron is detected by treating the residue with hydrochloric acid and adding potassium ferrocyanide, if iron is present a blue color is produced. Arsenic and antimony are detected by means of the Marsh apparatus. The sulphur is estimated by treating 1 gramme as in the analysis of gunpowder for sulphur.

**Charcoal.** — Light woods, such as alder, willow, poplar, and dog wood, furnish the best charcoal for the manufacture of gunpowder; it is lighter and more easily combustible than that from the harder woods and contains less potassium carbonate, a deliquescent salt, and other mineral impurities; hence, it absorbs less moisture and gives less residue when burned.

In the laboratory it is only necessary to determine whether the charcoal has been properly charred. For this purpose a determination of its moisture, volatile constituents and ash will be necessary.

*Moisture.* — Ten grammes of pulverized charcoal are heated in a porcelain crucible at 150° C, in a drying oven, for some time. The temperature should be raised gradually. It is allowed to cool in a dessicator and weighed.

*Volatile Matter.* — The crucible containing the dried charcoal is covered, placed in a clay crucible and surrounded with charcoal; the temperature is raised gradually; it is heated at a red heat for half an hour, allowed to cool, and weighed.

*Ash.* — Ten grammes of the charcoal in fragments are burned in a crucible, and the residue is weighed.

**Analysis of Gunpowder.** — A complete analysis of gunpowder includes the estimation of the ingredients, the determination of the nature of the charcoal, and the degree of purity of the ingredients. When powder has been damaged by moisture or otherwise, or when a powder of new or unknown manufacture is to be examined, it should be tested qualitatively for various impurities suggested by the particular cases under consideration, and the method of qualitative analysis to be adopted is determined by the results. A powder of known manufacture is examined qualitatively to determine the essential constituents, and the chlorides and moisture. The following is the most reliable process. The determination of the nitre depends upon its solubility in water, while charcoal and sulphur are insoluble. That of sulphur depends upon its easy oxidation by means of fuming nitric acid and potass-

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ium chlorate, forming sulphates, which are estimated by precipitation as barium sulphate.

Three samples of gunpowder are weighed in rapid succession (in order that the percentage of moisture determined for one shall be true for all) in the following manner: —

Two watch-glasses of equal size, with a clamp to fasten them together, are dried and weighed. A sample of powder (about 5 grammes) is then introduced and the whole reweighed, the difference is the weight of powder used. This sample (N) is placed in a beaker, of about 150 c. c. capacity, for the determination of the nitre. Another sample of powder about the same weight is introduced into the watch-glasses and weighed as before. This sample (S) is placed in a tall narrow beaker, of about 300 c. c. capacity, for the determination of the sulphur. A third sample of about the same weight is introduced into the watch-glasses and weighed as before.

This sample (M) is placed, together with the watch-glasses and clamp, in a drying oven, and dried at not exceeding 60° C., for about 24 hours. It is then removed from the oven, the crystals are clamped, and the whole placed in the scale case to cool. It is then re-weighed. The loss of weight determines the *moisture*.

Sample N is covered with water (about 50 c. c.), heated to 100° C., and allowed to settle. Meanwhile, two filters of the same size are prepared, and their difference in weight is determined. These are to form a double filter, the lighter is always placed underneath for convenience. A wide beaker, of about 300 c. c. capacity, is also weighed. The clear portion of the solution is decanted on the double filter, and the filtrate received in the weighed beaker. The residue is again treated with boiling water and the operation repeated. The residue is then washed from the beaker upon the filter, by means of boiling water being careful that every particle of residue is rinsed out of the beaker. The filtrate is evaporated to dryness in a water-bath, heated to 148° C. in an air-bath, and weighed. The increase of weight determines the *nitre* directly.

The residue is dried on the filter at 60° C. and weighed on the upper filter, balancing this filter by means of the lower. The loss of weight, minus the difference in weight of the two filters, and corrected for moisture, determines the *nitre* by difference

Sample S is covered with about 50 c. c. of fuming nitric acid, chemically pure, and brought to, and maintained at, a gentle ebulition. Small quantities of very finely pulverized potassium chlorate are added with caution, so that the liquid will not foam over, until a clear solution is obtained, being careful to add no more chlorate than is necessary for this purpose. If at any time there is a tendency to foam over, the beaker should be at once removed from the heat and allowed to cool. The solution is allowed to cool and hydrochloric acid is added in small quantities at first from a pipette, then as the action decreases it is poured in, until the amount of liquid in the beaker is about doubled. The whole is evaporated to dryness, redissolved in about 50 c. c. of water, made up to exactly 100 c. c., which is usually a sufficient and convenient quantity, filtered, and the amount of sulphur ascertained

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by means of a decinormal solution of barium chloride. A normal solution is prepared by dissolving 244 grammes of the crystallized salt, $Ba\,Cl_2 . 2\,H_2O$, in 1 litre of water; the decinormal solution is prepared by diluting a portion of this to ten times its volume.

To determine the sulphur, 5 c. c. of the solution containing the sulphates is put into a test tube and a portion of the decinormal solution of barium chloride is added from a burette and the tube well shaken; when the precipitate has settled, a drop or two more is added, and if cloudiness is produced, more is added until the addition of a drop of barium chloride no longer produces cloudiness. Having thus approximately determined the amount of barium chloride required to precipitate the sulphates, a series of solutions, of 5 c. c. of the solution of sulphates, containing greater and less amounts of barium chloride, is prepared. Thus, if 7.2 c. c. was found to be the approximate amount required, the series would contain 6.8, 7.0, 7.2, 7.4, 7.6, 7.8 c. c. The precipitates are allowed to settle and the tubes are tapped with the finger until the bubbles at the top disappear. A few drops of the solution of barium chloride are then poured in separate drops on a clean violet or ruby-colored glass plate, and a few drops of the solution of sulphates on another portion of the plate. A drop of one of the clear solutions in the test tubes, beginning usually with the lowest, is then put on the plate near one of each of the two solutions on the plate. One of the two drops thus placed is let into the drop of the solution of sulphates, the other into the drop of the solution of barium chloride, by means of a clean glass rod. If cloudiness appears in the sulphate solution take the next higher (to which more barium chloride has been added), and so on; if cloudiness appears in the solution of sulphates, take the next lower (to which less barium chloride has been added), and so on, until a point is reached where no cloudiness is produced in either solution.

From the reaction, $M_2\,SO_4 + Ba\,Cl_2 = Ba\,SO_4 + 2\,M\,Cl$, it is evident that every molecule of barium chloride detects one atom of sulphur; hence, every cubic centimetre of normal solution of barium chloride (since it contains a number of milligrammes of barium chloride equal to its molecular weight) is equivalent to a number of milligrammes of sulphur equal to its atomic weight, or 32. Every c. c. of a decinormal solution will then be equivalent to $\frac{32}{10}$ mg. sulphur. There were 100 c. c. of the solution of sulphates, 5 of which were used in the determination; hence, $\frac{32}{10} \times 20 \times$ the number of c. c. of barium chloride solution used, determines the weight of the *sulphur* in milligrammes.

The charcoal is determined (a) by ascertaining the percentage of nitre and sulphur in one sample of gunpowder and subtracting their sum from 100; or (b) by extracting the nitre from one sample and subtracting from the weight of the residue that of the sulphur found in an equal weight of another sample.

The chlorides are determined by redissolving the nitre, obtained in the estimation of nitre by the direct method, in the smallest quantity of water and proceeding as in the estimation of chlorides explained under Nitre.



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**Example : —**

| | | Milligrammes. |
|---|---|---|
| Weight of watch-glasses and clamp, | | 32514.9 |
| " " " " " " and powder M, | | 37521.8 |
| " " " " " " " " S, | | 37520.0 |
| " " " " " " " " N, | | 37519.3 |
| " " " " " " " " M dry, | | 37455.0 |
| " " Moisture, | | 66.8 |
| " " Powder M, | | 5006.9 |
| Percentage of moisture : — 5006.9 : 66.8 :: 100 : x | = | 1.33 per cent |
| Weight of powder N, | | 5004.4 |
| " " moisture : — 5006.9 : 5004.4 :: 66.8 : x | = | 66.8 |
| " " powder N, corrected for moisture, | | 4937.6 |
| " " beaker and nitre, | | 60393.7 |
| " " beaker, | | 56670.5 |
| " " nitre, direct, | | 3723.2 |
| Difference in weight of filters, | | 78.5 |
| Weight of powder N, corrected for moisture, | | 4937.6 |
| " " residue, 1295.2 — 78.5 | = | 1216.7 |
| " " nitre, by difference, | | 3720.9 |

4937.6 : 3723.2 :: 100 : x = 75.40 per cent. nitre, direct
4937.6 : 3720.9 :: 100 : y = 75.36 " " " by difference.

Amount of nitre solution = 70 c. c.
" tested = 7 c. c., required 0.65 c. c. $\frac{N}{100}$ Ag $NO_3$.
Weight of chlorides in nitre = $\frac{5.8 \cdot 5}{100} \times .65 \times 10 = 3.8$.

| | | |
|---|---|---|
| Weight of powder S, | | 5005.1 |
| " " moisture : — 5006.9 : 5005.1 :: 66.8 : x | = | 66.8 |
| " " powder S, corrected for moisture, | | 4938.3 |

Sulphate solution measures 100 c. c.
Amount tested = 5 c. c, required 7.4 c. c. $\frac{N}{10}$ Ba $Cl_2$.
Weight of sulphur = $\frac{3.2}{10} \times 7.4 \times 20$ = 473.6

4938.3 : 473.6 :: 100 : x = 9.59 per cent. sulphur.

| | | |
|---|---|---|
| 4937.6 : 1216.7 :: 4938.3 : x = weight of residue (S) | = | 1216.9 |
| " " sulphur S | = | 473.6 |
| " " charcoal | = | 743.3 |

4937.6 : 743.3 :: 100 : y = 15.03 per cent. charcoal.

| | | | |
|---|---|---|---|
| Per cent of sulphur | 9.59 | | 9.59 |
| " " " nitre (direct) | 75.40 | (by dif.) | 75.36 |
| " " " charcoal (a) | 15.01 | (b) | 15.03 |
| | 100.00 | | 99.98 |

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# SECTION 2.

## Gun Metal.

Gun metal, as formerly employed, was an alloy of 90.5 parts of copper and 9.5 parts of tin. The purest commercial qualities of copper and tin are always employed; a quantity of old gun metal is usually added, as it facilitates the mixing of the metals. Gun metal is no longer used in England or the United States for the construction of ordnance proper; however, the new Lyle Life Saving guns are being constructed of this material, Lake Superior copper and German tin being employed in the proportions of 92 parts of the former to 8 parts of the latter.

The impurities in gun metal are derived only from the metals employed in its fabrication or from the old gun metal added.

**Commercial Copper.** — The examination of the copper of commerce is limited to a qualitative determination of all the impurities, together with a quantitative estimation of the most important.

The impurities of most importance are sulphur, arsenic, tin, antimony and lead. The effect of these impurities upon the quality of copper is still imperfectly understood. Sulphur, even in minute quantities, seems to seriously injure the malleability of copper. Arsenic is almost invariably present, but does not appear to exercise any injurious influence. Tin in small proportions is said to increase the toughness of copper, but in large proportions renders it brittle. Antimony is a very objectionable impurity and is often present.

About 10 grammes commercial copper are dissolved in nitric acid (strength 22° Beaumé), the temperature is gradually raised to the boiling-point, and the boiling then continued for fifteen minutes. The solution is filtered, the residue and filter are dried, ignited and weighed. The residue consists of $Sn\,O_2$ and $Sb_2\,O_4$. It is treated with hydrochloric acid, and nitric acid is slowly added; when solution is complete it is boiled; after which a plate of pure tin is immersed, by which the ANTIMONY is precipitated as a black powder; it is dried at 100° C and weighed. The TIN is determined by difference.

To a portion of the filtrate sulphuric acid and alcohol are added; a white precipitate indicates LEAD. To another portion hydrochloric acid is added, a white, curdy precipitate indicates SILVER; it is soluble in ammonia. To a third portion ammonia is added, which precipitates the brown hydrate of IRON.

LEAD is determined quantitatively in the following manner. About 13 grammes copper are dissolved in nitric acid, and the solution is mixed with a small quantity of sodium phosphate; ammonia is added in excess, and the precipitate is purified from copper by washing with water containing a little ammonia. This precipitate is then dissolved in hydrochloric acid; the solution is rendered alkaline by ammonia, and treated with excess of sulphydric acid; the precipitated sulphides are washed

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thoroughly, and dissolved in dilute nitric acid; the solution is nearly neutralized by ammonia, and is digested with a small quantity of cupric hydrate or basic nitrate, which precipitates bismuth and iron if present. The solution is treated with sulphuric acid and alcohol to precipitate the lead as lead sulphate; it is filtered after a few hours, the precipitate is dried, ignited apart from filter, and weighed.

ARSENIC AND ANTIMONY are determined by the following method. About 13 grammes copper are dissolved in nitric acid, a small quantity of lead nitrate is added, equal to about 0.7 grammes of the salt, and subsequently an excess of ammonia and ammonium carbonate. The solution is filtered, the precipitate, consisting of lead oxide, carbonate, arsenate and antimonate, is thoroughly washed, and digested with a strong solution of oxalic acid, which dissolves the arsenic and antimony. The solution is filtered, the filtrate rendered alkaline by ammonia and sulphydric acid gas passed into it to saturation; the solution is again filtered, the filtrate diluted to 250 c. c., and slightly acidulated with hydrochloric acid. The vessel is exposed for a few hours to a temperature of 60° to 80° C. Antimony will be indicated by an orange precipitate, arsenic by a yellow one; if both are present the color will be intermediate.

The oxalic acid solution may also be placed in Marsh's apparatus, (*Fig.* 2, *Pl. V*), a piece of pure zinc immersed in it, and sulphuric acid added. When the air is completely expelled the escaping gas is kindled and a cold porcelain plate held over the flame. Arsenic and antimony will be indicated by a dark stain. Labarraque's Bleeching Liquid (sodium hypochlorite) dissolves the spot due to arsenic, but does not affect that due to antimony. The materials used must first be carefully tested for arsenic. If the jet is kindled before the air is expelled an explosion of the whole apparatus will take place.

To estimate the arsenic and antimony quantitatively, the precipitated sulphides, obtained in the first method for their detection, are oxidised with strong nitro-muriatic acid, the clear solution is mixed with ammonium chloride and excess of ammonia, and the arsenic is precipitated by magnesium sulphate as ammonio-magnesium arsenate. The precipitate is washed with water containing ammonia, dried, heated nearly to red heat, and weighed. It is thereby converted into $Mg_2 As_2 O_7$. The liquid filtered from this precipitate is slightly acidulated with hydrochloric acid and the antimony is precipitated by sulphydric acid as tri-sulphide; the precipitate is washed and dried, then placed, together with the filter, in a porcelain basin covered with a funnel, and fuming nitric acid poured upon it; the vessel is gently heated over a water bath. The resulting white mass is ignited and weighed, it consists of $Sb_2 O_4$.

SULPHUR is determined by dissolving 15 grammes of commercial copper in nitro-muriatic acid at a boiling temperature, thus converting it into sulphuric acid. Barium chloride is then added to precipitate the sulphuric acid as barium sulphate, proceeding as in the estimation of sulphur in the analysis of gunpowder.

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**Commercial Tin.** — The principal impurities in commercial tin are lead, copper, iron, antimony, and arsenic.

About 10 grammes are boiled in nitric acid (23° Beaumé), and the solution is filtered. To a portion of the filtrate, sulphuric acid and alcohol are added; a white precipitate indicates LEAD; it is dried at 120° C. and weighed; the lead is computed from the weight of lead sulphate thus obtained. To the solution filtered from the lead sulphate, ammonia is added; iron is precipitated as brown hydrate; the precipitate is washed, dried, ignited, and weighed as ferric oxide, $Fe_2 O_3$, from which the IRON is computed. In the solution filtered from the ferric hydrate, COPPER is indicated by the blue color of the solution. It may be estimated by either of the methods explained under commercial copper. ANTIMONY and ARSENIC are detected and estimated as explained under the same subject.

**Gun-Metal.** — The analysis of gun-metal consists in a determination of the essential constituents, tin and copper, and in a qualitative test for the presence of the principal impurities, followed, if necessary, by a quantitative estimation of those present. The principal impurities in gun-metal are lead, zinc, and iron. Lead is the most injurious of these; more than one per cent. would cause the alloy to be rejected.

Gun-metal is never homogeneous, on account of the separation of a white alloy containing a larger proportion of tin than gun-metal proper. Hence, great care must be taken in the selection of the sample for analysis. In castings of cannon three samples of equal weight are analysed, one taken at the breech, another at the trunnions and a third at the muzzle. To obtain the sample, a graver is preferred to a file, as the latter may introduce particles of iron.

A sample of 10 grammes of fine turnings is placed in a flask with a long neck, and acted upon by pure nitric acid, (22° Beaumé), and by sulphuric acid; the temperature is gradually raised to boiling, and the boiling continued for fifteen minutes. The fluid portion, together with the deposited stannic oxide, is put into an evaporating dish and evaporated to dryness on a water-bath; the dish is then heated until a portion of the cupric nitrate begins to decompose, liberating the black oxide; it is now set aside to cool. then moistened with nitric acid until the oxide disappears; the residue is diluted and the solution filtered; the residue is washed until it ceases to show an acid reaction. When dry, the stannic oxide is rubbed from the filter and poured into a porcelain crucible; the filter is incinerated on the cover, and the ashes are added to the contents of the crucible; the latter are moistened with nitric acid and ignited. The amount of TIN is computed from the stannic oxide, $Sn O_2$, thus obtained.

The filtrate is treated with a slight excess of sulphuric acid; the mixture is evaporated until the excess of sulphuric acid begins to pass off; it is then allowed to cool, is diluted with water containing one-fourth its volume of alcohol, and



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filtered on paper dried at 120° C. The precipitate is thoroughly washed and dried, then placed, with the filter, in a drying apparatus at 120° C, and heated until its weight becomes constant. The LEAD is computed from the lead sulphate thus obtained.

The copper is best determined by the gravimetric method. This gives the most accurate results, but requires considerable time and care in conducting the operations. For rapid work the volumetric method is preferred.

*Gravimetric Method.* — The filtrate from the lead sulphate, which should contain free sulphuric acid to prevent the precipitation of zinc, if present, is diluted in a beaker, heated to boiling, and a current of sulphydric acid passed through it, taking care to cover the vessel with a plate of glass to prevent oxidation. When all the copper is precipitated the conducting tube of the sulphydric acid apparatus is detached and left in the beaker; the liquid is filtered, the filtrate being received into an evaporating dish. Both the filter, during filtration, and the beaker containing the precipitate, must be carefully covered with a glass plate to prevent oxidation, and the filtration must be conducted as rapidly as possible. The precipitate is transferred as completely as possible to the filter, and is washed on the filter with cold water containing a few drops of sulphydric acid. If the last portions of liquid produce a turbidity in the filtrate, oxidation has taken place; therefore the operation is a failure and must be repeated. The precipitate is dried, rubbed from the filter into a weighed Rose's porcelain crucible, the filter is burned on the cover and the ashes are added to the contents of the crucible; a few centigrammes of flowers of sulphur are mixed with the contents. The crucible is covered with the perforated lid, to which a porcelain tube is attached connected with an apparatus for generating hydrogen, (*Fig.* 3, *Pl. V*). As soon as the hydrogen has expelled the air, the crucible is heated to redness. It is then allowed to cool in the atmosphere of hydrogen and weighed. The COPPER is computed from the cuprous sulphide, $Cu_2 S$, thus obtained.

*Volumetric Method.* — This method depends upon the reduction of an ammoniacal solution of a cupric salt by means of potassium cyanide, the color slowly disappearing in consequence of the formation of cupro-ammonium cyanide.

$$4\,Cu(NO_3)_2 + 8\,K\,CN + 4\,(NH_4 . HO) = 4\,Cu\,CN + 8\,KNO_3 + 2\,NH_4\,CN + 2\,NH_4\,C\,N\,O + 2\,H_2\,O.$$

The reaction represents the simple changes that take place, though, in reality, the changes are much more complex, the ultimate product being cupro-ammonium cyanide, $Cu\,CN . NH_4\,CN$.

The filtrate from the lead sulphate is evaporated to dryness, taken up with acidulated water, and ammonia added to precipitate the iron. The precipitate is allowed to settle, the solution is decanted and filtered, and the ferric oxide very carefully washed. The precipitate is washed by means of a wash-bottle, into a

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beaker, again dissolved in hydrochloric acid, and again precipitated as before. This operation is once more repeated; its object is to extract all the cupric oxide retained by the ferric oxide. The solution is made up to ½ litre, 50 c. c. of which are employed in the titration.

About 5 grammes potassium cyanide are dissolved in ½ litre of water. This solution does not keep well, and must be titrated once a week. The titration is performed by dissolving 1 gramme of chemically pure (best, electrolytically deposited) copper, in nitric acid, supersaturating the solution with ammonia and ammonium carbonate, and diluting to 1 litre. One c. c. = 0.001 gramme copper. Or, 7.867 grammes chemically pure blue vitriol, $Cu\,SO_4 . 5\,H_2O$, are dissolved, by the aid of water containing half its volume of ammonia and ammonium carbonate, and diluted to 1 litre. One c. c. = 0.002 gramme copper. These solutions are preserved for future use in well closed bottles.

From the reaction above, it is evident that each atom of copper requires two molecules of potassium cyanide to precipitate it; hence, 63.4 parts copper require $2 \times 65.1 = 130.2$ parts potassium cyanide. One hundred c. c. of the copper solution, or 50 c. c. of the cupric sulphate solution, are placed in a beaker, and the standard solution of potassium cyanide added till the tint is changed to faint lilac. It is then allowed to stand for 20 minutes, and, if the color does not disappear, a little more is added, and it is left to stand again. The number of c. c. determines the titration.

The estimation of the COPPER in the original solution is conducted in the same way. Multiplying the number of c. c. of potassium cyanide required, by the value in copper of 1 c. c., as determined by the titration, we obtain the amount of copper in 50 c. c. of the original solution. Multiplying by 10 gives the total amount in the original solution from 10 grammes gun-metal. Multiplying again by 10 gives the copper in 100 grammes, or the percentage.

The filtrate from the cupric sulphide, obtained by the gravimetric method, is oxidised by the addition of a little nitro-muriatic acid, or potassium chlorate, is boiled to expel the sulphydric acid, then saturated with ammonia until the color is reddish-brown, ammonium acetate added until the color is deep red, then neutral ammonium succinate, at a gentle heat, which precipitates the iron. The liquid is filtered when cold, the precipitate washed, first with cold water then with warm ammonia, dried, ignited, (the filter separately), moistened with nitric acid, and again ignited. The IRON is computed from the ferric oxide, $Fe_2O_3$ thus obtained. The iron may also be determined volumetrically as in the estimation of iron in the analysis of iron ores and commercial iron. (*p.* 77, *et seq.*)

The filtrate from the ferric hydrate, is evaporated to concentrate it; crystallized sodium carbonate is added gradually, with continuous stirring, until all effervescence ceases, keeping the vessel covered to prevent loss. The liquid is boiled, then

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filtered; and the precipitate is washed with boiling water, dried, heated to a red heat (the filter ignited separately), and weighed. The ZINC is computed from the zinc oxide, Zn O, thus obtained.

Each metal, in this process, must be *completely* precipitated from the successive filtrates; the filtrates must therefore be carefully tested for the metal last separated, and if traces are found, more of the proper reagent is added to effect the complete precipitation.

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## SECTION 3.

### IRON.

Iron occurs native, generally in grains disseminated through igneous rocks, sometimes in masses weighing a ton. In meteoric iron it is usually alloyed with nickel. Its most abundant ores are the following, which, when pure compounds, contain the annexed percentages of iron by calculation: — siderite or spathic iron ore, $Fe\,CO_3$, containing 48 per cent. of iron; hematite or specular iron ore, $Fe_2\,O_3$, containing 70 per cent. of iron; limonite or brown hematite, $2\,Fe_2\,O_3\,.\,3\,H_2\,O$, containing 59.8 per cent. of iron; magnetite, $Fe_3\,O_4$, containing 72.4 per cent. of iron.

These ores generally contain clay and other impurities, the most important of which are lime, magnesia, silica, alumina, phosphorus, sulphur, manganese and organic matter.

It is necessary to determine the iron and the impurities in an ore, in order to determine the value of the ore, its proper method of treatment, and the quality of the iron obtainable. If the gangue, as a whole, be either acid or basic, it will be infusible; whereas it should have about the same degree of fusibility as the cast-iron, in order that they may pass the blast-pipes together, the slag thus protecting the iron from oxidation.

To produce this fusibility of the slag a flux is added. If the gangue is basic, that is, contains much limestone, which will leave lime under the action of heat, an acid flux, such as silica, is added; if it is acid, that is, contains much siliceous matter, a basic flux, such as limestone, is added. The slag is principally calcium silicate. In case the gangue is siliceous, there would also be a loss of iron if no flux were added, for part of the iron would combine with the silica forming a fusible slag of iron silicate.

The most objectionable impurities, affecting the quality of the resulting iron, are sulphur and phosphorus, the former rendering iron brittle when hot (red-short or hot-short), the latter rendering it brittle when cold (cold-short). Manganese affects the quality of the iron produced, but its action is imperfectly understood. When added to cast-steel only traces of it pass into the steel, the bulk of it going into the slag, apparently carrying the sulphur and phosphorus with it.

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*Analysis of Iron Ores.*

**Selection of Sample.** — A considerable quantity of ore is broken into small fragments, a shovel full of which is pulverized in a large iron mortar; this is then spread out on a level surface in the form of a circle; one quadrant is selected and pulverized to a greater degree; one quarter of this is taken, and so on, until about 30 grammes remain, which will pass through a sieve with 25 meshes to the centimetre. Coarser particles, which will not pass through the sieve, must be further pulverized and added to the finer material. The sample is then dried at 110° to 120° C. to remove hygroscopic moisture, and is now ready for assay.

**Assay of Iron Ores.** — The assay of iron ores is useful in testing, on a small scale, a stochiometrically calculated charge for the iron furnace. It consists in a fusion of the ore in a crucible, in contract with charcoal, by means of which the ore is reduced to a button of metallic iron, the other constituents combining to form a slag. Since much of the carbon, manganese, copper, cobalt, nickel, etc., of the ore is also present in the button, the latter does not represent the pure iron present, but the impure pig-iron obtainable from the ore. The button will not separate completely from the slag unless the latter has the proper fusibility, and, as the constituents of the gangue seldom possess this property, fluxes are usually added. The proper kind and the best proportions are determined empirically, by making a number of assays with charges of various amounts of flux. The flux is determined approximately by the mineralogical character of the gangue: —

| | Parts flux to one part ore, by weight. |
|---|---|
| A. For ores with *unknown* gangue. Mixture of equal parts white glass (free from Fe and Pb) and calcium carbonate..... | 0.5 |
| B. For ores with *quartz* gangue. | |
| *a.* Aluminous ores. — Mixture of one part glass and four parts Ca $CO_3$..... | 0.5 to 0.7 |
| *b.* Non-aluminous ores. — Mixture of one part clay and two parts Ca $CO_3$..... | 0.5 to 0.7 |
| C. For ores containing much *clay*. | |
| *a.* Siliceous gangue. — Ca $CO_3$..... .... | 0.25 to 0.4 |
| *b.* Less siliceous gangue. — Mixture of one part glass and two parts Ca $CO_3$..... | 0.4 to 0.6 |
| D. For ores with *calcareous* gangue. Mixture of one part clay (free from iron) and two parts quartz..... ..... | 0.3 to 0.5 |

About 2 grammes of ore are mixed with the proper flux and placed in the centre of a charcoal-lined crucible, care being taken to leave no ore adhering to the sides.

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The crucible is then completely filled with dry powdered charcoal, and covered with a circular piece of charcoal pierced with holes for the escape of the gases. The crucible is then placed in a furnace, surrounded with charcoal, and heated gradually to a red heat. It is allowed to remain so for 1½ hours, when it is taken from the furnace while still hot, allowed to cool, the cover removed after cooling, and the button extracted. The slag is pulverized and any particles of iron it may contain are extracted by means of a magnet, and weighed with the button.

With a well selected charge, the slag is light colored and the button compact and light gray or white in the fracture. With a charge too basic, the slag is earthy and the button soft and filled with scales of graphite. With a charge too acid, the slag is green or black, and the button tough and malleable.

A violet or brown color in the slag indicates *manganese*; sink holes in the upper surface of the button and a white surface of fracture indicates *sulphur*; a smooth outer surface of the button, a white surface of fracture and great brittleness indicate *phosphorus*.

**Analysis in the Wet Way.** — For this purpose the ore is further pulverized by rubbing in an agate mortar until it ceases to feel gritty.

**Determination of Volatile Matter.** — It is not generally necessary to determined water, organic matter, carbon dioxide, etc., separately; but these may be determined collectively as *volatile matter*.

A platinum crucible is heated to whiteness, cooled, and weighed, 10 grammes of the substance are placed in it and heated to redness for one hour. The crucible is removed from the heat, covered, allowed to cool, and weighed.

**Solution.** — Most ores are sufficiently decomposable by acids, especially by concentrated hydrochloric acid, but the ore must be finely pulverized, and the acid of proper strength. It is also well to gently and continuously shake the solution, while it is being warmed at 50° C. in case of hydrochloric acid, at 100° C. in case of sulphuric acid. In case the ore contains organic matter, roasting should precede solution.

In case the residue, if any, is colored, it is filtered from the solution, washed, dried, and incinerated with the filter in a platinum dish. If it still remains red, some of the iron has remained undissolved. It is then fused in a platinum dish with five times its weight of potassio-sodic carbonate, until gas bubbles no longer escape, dissolved in water, transferred to a porcelain dish, carefully treated with acid to dissolve the metals, evaporated to dryness, moistened with acid, and, after addition of water, filtered from the silica. The filtrate is added to the original solution.

**Determination of the Iron.** — There are two principal volumetric methods for the determination of the iron: the *potassium permanganate method*, and the

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*stannous chloride method.* The latter is preferable for ores containing little ferrous oxide, or for ores more easily soluble in hydrochloric than in sulphuric acid, even though they contain some ferrous oxide.

**1. Potassium Permanganate Method.** — Potassium permanganate in contact with ferrous salts oxidises the latter to ferric salts, becoming itself thereby deoxidised and therefore decolorized; the instant the oxidation is complete, however, an additional drop of the permanganate colors the solution deep red. The chemical changes are here represented: —

$$10\,Fe\,SO_4 + 2\,K\,Mn\,O_4 + 8\,H_2\,SO_4 = 5\,Fe_2\,(SO_4)_3 + K_2\,SO_4 + 2\,Mn\,SO_4 + 8\,H_2\,O.$$

*Preparation and Titration of Permangate Solution.* — About 5 grammes crystalized potassium permanganate are dissolved in one litre distilled water, the residue is allowed to settle, and the clear liquid poured into a ground-glass stoppered bottle.

The titration is performed by means of oxalic acid, a warm solution of which is decomposed rapidly by the permanganate: —

$$5\,(C_2\,H_2\,O_4\,.\,2\,H_2\,O) + 2\,K\,Mn\,O_4 + 3\,H_2\,SO_4 = 10\,CO_2 + K_2\,SO_4 + 2\,Mn\,SO_4 + 18\,H_2\,O.$$

From the first equation above it is evident that 10 Fe (560 parts by weight) require 2 K Mn $O_4$; and from the second, that 5 molecules oxalic acid (630 parts by weight) require also 2 K Mn $O_4$; hence, 630 parts oxalic acid are equivalent to 560 parts of iron, or 9 of the former to 8 of the latter.

The titration is performed by dissolving about 0.3 gramme oxalic acid in 200 c. c. distilled water, adding several c. c. concentrated sulphuric acid, heating to about 60° C., and then adding permanganate solution drop by drop. At first the solution is decolorized slowly, but soon each drop is decolorized suddenly, until, finally, a drop colors the entire solution red. The number of c. c. of permanganate solution used is noted. The oxalic acid used is computed as iron, by multiplying by $\frac{8}{9}$, as above explained, and this, divided by the number of c. c. of permanganate solution used, gives the value in iron of each c. c. This solution of permanganate keeps well in a glass-stoppered bottle, in the dark, and need be tested but once a month.

*Estimation of Iron.* — From 0.5 to 0.75 gramme ore are dissolved in sulphuric acid (equal parts of sulphuric acid and water) as already explained. In case the ore is decomposable only by hydrochloric acid, the solution is evaporated in a water-bath, with addition of concentrated sulphuric acid, until nearly or quite all the hydrochloric acid has been expelled; the solution is then diluted.

The next step is the reduction of the ferric oxide present to ferrous oxide by means of a small piece of zinc free from iron. The zinc is enclosed in a platinum-wire net and suspended in the solution; the latter is heated in a stream of carbon

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dioxide by means of the apparatus represented in *Fig.* 4, *Pl. V.* A, contains a carbonate to which hydrochloric acid is added, the carbon dioxide generated is washed in B and then passes into C which contains the iron solution and zinc. This current of carbon dioxide, by excluding the air, prevents reoxidation of the reduced ferric oxide. When the zinc is dissolved, or the solution decolorized, a drop is tested with potassium sulpho-cyanide solution, and if a red coloration results more zinc is required, otherwise the solution is poured from the residue of the zinc, if any, allowed to cool, and potassium permanganate solution added from a burette with a glass stop-cock. The number of c. c. required, multiplied by the value of one c. c. in iron, gives the amount of iron.

**2. Stannous Chloride Method.** — Stannous chloride in contact with ferric salts reduces the latter to ferrous salts, thereby changing the yellow solution to a colorless one. Heat assists this change, but even with the application of heat it is difficult to determine the point at which the reaction is complete; hence, the excess of stannous chloride used must be determined, and this is accomplished by means of a solution of iodine in potassium iodide. Starch solution is added to the iron solution; it is not affected by the iodine so long as any stannous chloride remains, but as soon as the latter disappears the solution turns deep blue, due to the formation of a compound of starch and iodine.

*Preparation and Titration of the Solutions* — The iodine solution is prepared by dissolving 20 grammes potassium iodide in one litre water, and adding 10 grammes pure iodine.

The stannous chloride solution is prepared by heating pure tin (Banca tin) in an old porcelain dish to fusion. It is then removed from the heat and rubbed with a porcelain pestle till it hardens and remains in a finely-divided state. An excess of this is warmed and treated in a capacious flask with hydrochloric acid (ordinary C. P., sp. gr. 1.12) till gas no longer escapes; the resulting concentrated solution is poured off, diluted with nine times its volume of dilute hydrochloric acid (one part H Cl to two parts water), and placed in the vessel *a*, (*Fig.* 5, *Pl. V*), for preservation. *c* contains dilute hydrochloric acid, in which is suspended through the plaster of Paris plate *h*, the flask *d*, containing fragments of marble and having a small opening at bottom. When *a* is filled with the solution, the cork is inserted with its glass tubes, the clamp *g* is opened and air blown in at *b* until *f* is filled, then the clamp is closed. *c* is now attached, the cork of *a* is raised a little to allow the carbon dioxide to displace the air in *a*, and the cork again inserted. The pressure of the carbon dioxide generated in *d* forces out the acid; now when *g* is opened, and some solution run off, the acid again enters *d*, generating carbon dioxide, which replaces the solution removed, and so on.

Some of the solution is run into a Mohr's burette, and by means of an Erdmann's float exactly 2 c. c. are run from the burette into a beaker, diluted with 5 c. c. water

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and a few drops of starch solution* added. From a second burette with glass stopcock, iodine solution is added until the liquid is colored permanently blue. The burette is read and the number of c. c. stannous chloride corresponding to one c. c. iodine solution is calculated.

To titrate the stannous chloride solution, 10.04 grammes soft, well cleaned iron wire, containing 10 grammes pure iron, are dissolved in hydrochloric acid; potassium chlorate is added in small portions, and the solution kept at gentle ebullition for several hours, until the odor of chlorine has *entirely* disappeared. A drop is then tested with potassium ferri-cyanide; if a blue coloration results, there is still some unconverted ferrous chloride and the operation is continued; but in case of its entire absence, the cold solution is diluted with distilled water to one litre and preserved in a glass-stoppered bottle for use. It contains in 100 c. c. one gramme iron and constitutes a standard solution of iron.

Fifty c. c. of this standard solution (containing 0.5 gramme iron), after acidification with a little hydrochloric acid, are heated to boiling in a beaker. Stannous chloride solution is carefully added, with stirring, and more and more slowly as the decolorizing proceeds, until it is completed. It is allowed to cool, a little starch solution is added, then iodine solution form a burette till the reaction seems permanent. The number of c. c. iodine solution, multiplied by the value of one c. c. in stannous chloride, gives the excess of stannous chloride used (it should not be above a few tenths c. c.); this is subtracted from the total amount of stannous chloride solution used, corresponding to 0.5 gramme iron. The amount of iron corresponding to one c. c. stannous chloride solution is then computed and recorded.

*Estimation of the Iron.* — From 0.7 to one gramme ore is dissolved in hydrochloric acid as already explained, diluted to 50 c. c. and heated to boiling. In case of ores containing only *ferric* oxide (hematite and limonite), the stannous chloride can be added directly; but in case of ores containing *ferrous* oxide, this must first be converted into ferric oxide by means of potassium chlorate as explained above, care being taken to test with potassium ferri-cyanide whether the conversion is complete, and also to remove completely the oxidising agent by long continued boiling. The addition of stannous chloride proceeds as explained in the titration of it: to the boiling hot solution of the ore, stannous chloride is added until it is decolorized; it is then allowed to cool, a few drops of starch solution are added, and the excess of stannous chloride determined by means of iodine solution. The difference determines the amount of stannous chloride required, from which the amount of iron present may be computed.

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* **Preparation.** — Powdered starch flour is mixed with about 100 c. c. water, heated to boiling with continued stirring, allowed to cool, the clear solution poured off and preserved with a few drops of alum solution in a stoppered bottle.



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**Separation of Ferrous and Ferric Oxide.** — Two samples are dissolved in the apparatus represented in *Fig.* 4, *Pl. V;* in one the *ferrous* oxide is determined by the permanganate method, in the other the *ferric* oxide by the stannous chloride method. Or, the total iron may be determined by either method, and either the ferrous or ferric oxide by the method relating thereto; the other being then determined by difference.

**Determination of Silica, Alumina, Magnesia, Calcium, and Manganese, in the absence of other heavy and earth metals.** — One to two grammes of ore are dissolved in warm hydrochloric acid as already explained, and, if the ore contains ferrous oxide, nitric acid is added, the solution evaporated to dryness, the residue warmed with some concentrated hydrochloric acid, diluted with water till all salts are dissolved, filtered, and the residue carefully washed with pure water. The residue is dried on the filter, the filter burnt and then ignited in a platinum crucible, at first gently, then strongly. If the residue is white it is weighed as SILICA, $SiO_2$. If it is colored it is fused with five times its weight of potassio-sodic carbonate and washed on a filter. The filtrate is added to the solution previously obtained, while the residue of silica is washed till pure, ignited and weighed.

In case the solution contains *ferrous* chloride, (determined by testing a drop with $K_4 Fe C_6 N_6$ on a porcelain cover — indicated by a blue coloration), it is boiled with nitric acid as before. The ferric chloride solution, not too concentrated, after cooling is neutralized by adding sodium carbonate solution very slowly and carefully, as far as is possible without producing a precipitate. Then, to one gramme ore dissolved, ½ c. c. concentrated acetic acid and ½ gramme sodium acetate are added, and the solution heated in a porcelain dish to boiling. The precipitate, consisting of ferric oxide, alumina, and phosphoric acid, is allowed to settle, the colorless solution is decanted and passed through a filter, and the precipitate is washed by continued decantation with hot water containing sodium acetate, the last washings being tested for chlorine. For the determination of the alumina in the precipitate, it is dissolved in the smallest quantity of hydrochloric acid, heated in a porcelain dish to boiling, ammonia is added in slight excess, the solution boiled, allowed to settle, filtered, and the precipitate washed so completely with boiling water, that, after acidification with nitric, acid not the slightest cloudiness is produced in the washings by silver nitrate. After drying, the precipitate is removed as completely as possible from the filter, the filter burnt, and the precipitate ignited in a porcelain crucible until the weight remains constant, and weighed. This is the weight of the ferric oxide, alumina, and phosphoric acid. The sum of the weights of the first and last, determined by methods given, subtracted from the weight of the residue, gives the ALUMINA, $Al_2 O_3$.

To the filtrate obtained in the precipitation of the alumina, etc., several drops of bromine are added, the solution is well stirred, several drops of sodium carbonate

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solution are then added, but not to complete neutralization, the solution is warmed slowly to boiling till the bromine is expelled, filtered, the dark brown precipitate washed with water containing 1 per cent. hydrochloric acid, dried, ignited strongly in a platinum crucible (after separately burning the filter), and weighed as manganoso-manganic oxide, $Mn_3 O_4$, from which the amount of MANGANESE oxide, Mn O, may be computed.

To the solution filtered from the manganese, ammonium chloride is added in such quantity that ammonia produces no precipitate, more ammonia is then added and finally ammonium oxalate in excess: the precipitate is allowed to stand 12 hours, it is then filtered, and washed in the glass and on the filter. The precipitate of calcium oxalate is washed into a beaker, the filter washed with hot sulphuric acid, and the washings and precipitate, after addition of more sulphuric acid, are warmed to 60° C. producing a clear solution. Permanganate solution is then added from a burette in the manner above explained. The value in iron of one c. c. permanganate solution has been determined, and this, multiplied by the number of c. c. used, gives the equivalent in iron; but 8 parts iron correspond to 9 parts oxalic acid, one part of oxalic acid, $C_2 H_2 O_4$, contains $\frac{4}{7}$ part of the acid oxide radical, $C_2 O_3$, and 9 parts of the acid oxide radical combine with 7 parts calcium oxide to form calcium oxalate; hence, the equivalent in iron, multiplied by $(\frac{8}{9} \times \frac{4}{7} \times \frac{7}{5} = \frac{1}{2})$, gives the LIME.

To the solution filtered from the calcium oxalate, sodium phosphate solution is added in the cold to excess, the solution is stirred without touching the sides of the beaker, allowed to stand for 12 hours, filtered, the precipitate washed on the filter with dilute ammonia (one part ammonia to three parts water) until no effect is produced upon addition of nitric acid and silver nitrate, dried, ignited in a covered crucible, at first gently, then to strong ignition, the cut-up filter being burned on the cover of the crucible and the ash added to the precipitate, and the latter again ignited and weighed. The precipitate is magnesium pyrophosphate, $Mg_2 P_2 O_7$, from which the MAGNESIA, Mg O, may be computed.

**Determination of Phosphorous.** — From one to three grammes ore are taken. To every one gramme ore a mixture of six c. c. nitric acid (sp. gr. 1.2) and six c. c. hydrochloric acid is used, in which the ore is digested with the aid of heat, more acid being added if necessary; the solution is then evaporated to dryness in a water-bath. The residue is moistened with 5 c. c. nitric acid to every 1 gramme ore, warmed, diluted with an equal quantity of water, filtered, and washed with as little water as possible. The solution is evaporated to at least twenty c. c. for every one gramme of ore.

A solution of potassium molybdate is then prepared by dissolving 50 grammes in 150 c. c. water, adding a solution of 12.5 grammes tartaric acid in 50 c. c. water, pouring the mixture into 160 c. c. nitric acid (sp. gr. 1.2), boiling and filtering.

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Twenty-five c. c. of the molybdate solution are warmed to 100° C. in a water-bath, in a second water-bath the iron solution is heated to the same temperature; the latter is added to the former, and the heating continued for 20 minutes. (A small portion of the solution is tested by adding more warm molybdate solution to see if any farther precipitation results). A filter is clamped between two watch-glasses, dried at 120° C. in the air bath, and the whole weighed. The precipitate is placed on this filter, washed with water containing two volume-per-cent. of nitric acid till all iron is removed, then three or four times with alcohol. It is then dried between the watch-glasses at 120° C. for 25 minutes, allowed to cool in an exsiccator and weighed. It consists, after drying, of potassium phospho-molybdate, $3\ K_2\ O\ .\ P_2\ O_5\ .\ 22\ Mo\ O_3$, from which the percentage of $P_2\ O_5$ may be computed.

**Determination of Sulphur.** — A solution of 10 grammes pure potassium chlorate (free from $H_2\ SO_4$) in 200 c. c. water is prepared and poured upon five grammes finely-pulverized ore in a capacious beaker. The solution is heated to boiling, 60 c. c. hydrochloric acid are slowly added, keeping up the boiling. The boiling is continued for one hour, more acid being added if necessary, and then the solution is evaporated to dryness in a water-bath. The residue is moistened with 10 c. c. hydrochloric acid and 30 c. c. water, and warmed in the water-bath till the ferric chloride is dissolved. The solution is then diluted with 20 c. c. water and filtered. [If the residue contains calcium sulphate it is warmed with 5 c. c. hydrochloric acid and 15 c. c. water, in a boiling hot water-bath, for 2 hours, with continued stirring, the solution filtered and the residue washed with warm water without bringing it on the filter, the washings and filtrate being added to the filtrate previously obtained].

The filtrate is heated to boiling, 2 to 4 c. c. barium chloride solution are added, the solution is kept at boiling for a few minutes, allowed to cool, 10 c. c. ammonia (sp. gr. 0.95) are added, the whole well stirred and allowed to stand in a warm place for at least 24 hours. The clear liquid is poured off through a small filter, the precipitate washed in the glass, first with cold, finally with hot water, till silver nitrate no longer produces cloudiness in the washings. It is then washed upon the filter with hot water, dried, ignited in a porcelain crucible (the filter separately), and weighed. It consists of $Ba\ SO_4$, from which the percentage of sulphur is computed.

**Determination of Manganese.** — This process consists in precipitating the manganese as manganese dioxide, $Mn\ O_2$, reducing and redissolving this precipitate by treatment with an acid solution of a ferrous salt, the strength of which is known,

$$Mn\ O_2 + 2\ Fe\ O = Mn\ O + Fe_2\ O_3,$$

determining the amount of iron required for reduction, by estimating the amount

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remaining in the solution by volumetric analysis, and subtracting this from the total amount used.

*Reagents.* — 1. Calcium hypochlorite solution. Fifteen grammes " chloride of lime " (bleaching powder) are dissolved in one litre of water in the cold, the solution is filtered, if necessary, and preserved in a glass-stoppered bottle. 2. — Calcium carbonate. A solution of calcium chloride is precipitated by sodium carbonate at 80° C., and the precipitate is washed and dried. 3. — Acid solution of ferrous sulphate. Fifty grammes crystallized green vitriol are dissolved in a mixture of 250 grammes English sulphuric acid and 750 grammes water. 4. — Potassium permanganate solution. Prepared as in the estimation of iron, its value in iron being multiplied by 0.491 to obtain its value in manganese by the present method, since, from the reaction above, a molecule of Mn O containing one atom Mn (55 parts by weight) converts two atoms Fe (112 parts by weight) into the form of ferric oxide. Hence, 112 : 55 :: 1 : 0.491, or one part iron is equivalent to 0.491 parts manganese.

In a beaker of 500 c. c. capacity 0.5 gramme ore rich in manganese, or 2 grammes ore poor in manganese, are dissolved by means of the smallest quantity of hydrochloric acid (nitric acid is added in case ferrous oxide is present), and evaporated in a water-bath to a syrupy consistence, only sufficient water to dissolve the ferric chloride with a yellow color being carefully added. To the cold solution, calcium carbonate is added with continued stirring, till the solution has acquired an orange color, then 50 to 60 c. c. calcium hypochlorite solution, sufficient boiling water to warm the solution to 70° C., and finally, for ores poor in iron 1.2 grammes, for ores rich in iron 1.6 grammes, calcium carbonate, previously weighed. A slight excess of calcium carbonate is necessary ; hence, if no particles are left undissolved, a little more is added, but care must be taken to avoid a large excess. The iron and manganese are precipitated ; the liquid is stirred, the precipitate allowed to settle, filtered, and washed till no chlorine can be detected by starch and potassium iodide. The filter and precipitate are placed in the beaker previously used for the precipitation, and which still contains adhering particles of precipitate, and 50 c. c. ferrous sulphate solution are added. Reduction and complete solution follow, the solution is diluted with three times its volume of water, and titrated by means of the permanganate solution. A volume of ferrous sulphate solution exactly equal to that used for dissolving the precipitate is also titrated with permanganate solution. The difference in c. c. determines the amount of iron required to reduce the manganese dioxide. Multiplying by 0.491, as explained above, determines the manganese.



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| | Lake Superior Red Specular Ore. | Pilot Knob. Mo., Specular Ore. | Kentucky Limonite | Lake Champl'n Ore. | Hanging Rock, O., Blue Ore. |
|---|---|---|---|---|---|
| Volatile Matter | 0.77 | | 10.21 | | 30.76 ($CO_2$ |
| $Fe_2O_3$ | 90.52 | 84.33 | 69.93 | } 95.99 | 13.51 |
| Fe O | | 0.15 | | | 42.48 |
| Mn O | trace | | | 0.10 | 0.13 |
| $Al_2O_3$ | 1.39 | 2.19 | 3.12 | 2.00 | 0.59 |
| Ca O | 0.70 | 0.21 | 1.53 | 0.52 | 3.43 |
| Mg O | 0.42 | 0.14 | 1.62 | 0.60 | 1.00 |
| $P_2O_5$ | 0.26 | 0.04 | 0.24 | 0.10 | 0.35 |
| $SiO_2$ | 5.89 | 13.27 | 13.45 | 0.64 | 7.52 |
| S | 0.05 | | | 0.10 | 0.15 |

*Analysis of Commercial Iron.*

Commercial iron usually falls under the three classes, cast-iron, wrought-iron, and steel. The first contains the largest proportion of carbon, and is represented by $Fe_5C$, approximately; steel is represented by $Fe_{14}C$, and wrought-iron is nearly pure iron, although it generally contains a small percentage of carbon.

The most important impurities in commercial iron are sulphur, phosphorus, silicon and manganese. Sulphur and phosphorus have a deteriorating effect on the strength and tenacity. Manganese (and carbon and silicon in a less degree) diminishes the effect produced by phosphorus and sulphur. Carbon modifies this action. Steel with 0.5 per cent. C and upwards and at the same time more than 0.1 per cent S will be red-short, and with more than 0.1 per cent. P cold-short; even 0.03 per cent. renders steel useless for tools of fine temper. If much manganese is present the percentage of P may rise higher, but such steel cannot be tempered.

The effect of silicon is far less marked and is modified by carbon; 2 per cent. is found in good rails. Si and Mn prevent extrusion of gases and hence prevent honey-combing in the cooling of molten steel. C and Si, 0.5 to 1.0 per cent., produce hot and cold-shortness.

**Sample for Analysis.** — The sample is obtained by means of a hard English file and collected on paper; or by pulverization in a hard steel mortar. The principal constituents to be determined are iron, carbon (free and combined), silicium, phosphorus, sulphur and manganese.

The iron is determined as in iron ores.

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**Total Carbon.** — One to two grammes cast-iron, two to three grammes steel, or three to five grammes wrought-iron are employed. Three hundred grammes cuproammonium chloride are dissolved in one litre water. For every one gramme iron 50 c. c. of this solution are measured into a beaker, the iron added and the liquid stirred. It is then warmed gently, continuing the stirring, until all iron and separated copper are dissolved, which requires about 25 minutes; the carbon remains undissolved.

A funnel is constructed of a glass tube of 15 mm. diameter and 75 mm. length, the end of which is drawn out to an interior diameter of 4 mm. The point of the funnel is filled with glass particles, and over this is packed previously ignited and finely-fibrous asbestus. The solution is passed through this filter, the first filtrate being tested for solid particles by diluting with hydrochloric acid to render it transparent. The residue of carbon is then placed in the filter and washed with cuproammonium chloride solution and afterwards with water till silver nitrate produces no cloudiness in the washings.

The apparatus, *Fig.* 6, *Pl. V*, is then arranged. *a* is a heating-flask of 300 c. c. capacity; *b* a filling-funnel with glass stop-cock; *c* a tube filled with sodium hydrate, and fastened air-tight into *b* by means of a cork; *d* a wash-bottle of 100 c. c. capacity, ⅓ full of concentrated sulphuric acid, whose connection with *a* may be interrupted by means of the clamp; *e* a calcium-chloride tube; *f* a caustic potash apparatus, with a calcium chloride tube, *g*, attached; *h* is an aspirator, a jar without bottom, of 8 litres capacity, resting in a low dish containing water, and having a bent tube, with glass stop-cock, fitting air-tight into its cork. After opening the stop-cock the outer vessel is filled with water, then by suction on the bent tube the jar is filled, after which the stop-cock is closed. The tube *i*, connected with the aspirator, contains fragments of potassium hydrate in the bulb, and of calcium chloride in the stem. To fill the potash apparatus 15 grammes KHO are dissolved in 25 c. c. water, the end of the apparatus next to the larger bulb is inserted in the solution, and the solution is drawn in by suction until the lower three bulbs are nearly filled, the inserted end being then carefully wiped. The degree of filling, as well as the proper position of the apparatus when in use, is shown in *Fig.* 7, *Pl. V*. In the bulb of the tube *g* a small piece of cotton is placed, and upon this several pieces of caustic potash; in the stem, calcium chloride is placed, covered with a loose stopper of cotton. The tube is then connected air-tight, by means of a dry cork, with the small end of the potash apparatus.

The funnel and its carbon are placed in *a*, the stop-cock *b* is closed; that of the aspirator is then carefully opened to test the joints: no air-bubbles should rise in *d* or *f* after equilibrium is established. The potash apparatus and the tube *g* are removed and weighed; several litres of air free from carbon dioxide are meanwhile drawn through the apparatus, the caoutchouc tube of the aspirator being attached to the tube *e*, and the stop-cock *b* opened, *c* remaining on the funnel. The weighed

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potash apparatus is inserted in place, without connecting with the aspirator, the tube *c* is removed, and 10 c. c. of a solution of chromic acid, composed of 30 grammes acid to 100 c. c. water, is carefully allowed to pass through *b* into *a*. The stop-cock of *b* is closed, 50 c. c. concentrated sulphuric acid are placed in the funnel, a small quantity of which is passed carefully into the chromic acid solution, shaken up, and the rest of the acid slowly added. The stop-cock of the funnel is closed and *a* is gently warmed. The clamp between *a* and *d* is of course open during these operations. The evolution of gas is regulated so that two or three bubbles pass through *d* per second. In about 1½ hours the evolution of gas ceases, the solution is then heated to boiling for several minutes, the tube *c* is again placed on *b*, the clamp between *a* and *d* closed, the heat removed and the stop-cock of *b* opened. Meanwhile, the aspirator is again attached to *g*, and when *a* has become cool, the clamp and stop-cock of the aspirator are opened and 4 litres air are drawn through the apparatus. The potash apparatus is removed and again weighed, its increase in weight being the weight of the carbon dioxide, $CO_2$, evolved, from which the amount of carbon can be computed.

**Graphite.** — The same quantity of iron is employed as in the determination of the total carbon. It is dissolved in dilute hydrochloric acid, heated to boiling, the residue collected on an asbestos filter as before, and washed with hot water till silver nitrate no longer produces cloudiness in the washings. It is then washed with dilute caustic potash five times or more, till the filtrate is colorless, then with alcohol, then with ether, and finally with water. The graphite is determined by oxidation in the apparatus and by the method used for determining the total carbon.

The difference between the total carbon and the free carbon, or graphite, determines the *combined carbon*.

**Color Test for Carbon in Iron and Steel.** — The iron to be tested is finely divided by filing, pulverization in a steel mortar, etc. Test-tubes, 120 mm. in length and 15 mm. in diameter, are cleaned with filter paper. 0.1 gramme wrought iron or steel, or 0.05 gramme white pig iron, is carefully weighed, put into one of the tubes, and 2.5 c. c., or more, of nitric acid (sp. gr. 1.2) are added. For iron containing 0.25 per cent. carbon 2.5 c. c. are used for each 0.1 gramme, for iron containing 0.30 per cent. 3 c. c., for iron containing 0.50 per cent. 3.5 c. c., and finally for iron containing 0.70 per cent. 4.0 c. c. For steels with more carbon, or for pig iron 5 c. c. for every 0.1 gramme. The acid may be measured off in a little measuring flask of 10 mm. diameter and 75 mm. length, graduated to ½ c. c.

The tubes are covered with small watch-glasses (23 mm. in diameter), and put into a cylindrical copper vessel, 100 mm. high and 120 mm. in diameter, covered with a copper plate provided with a thermometer and holes for the tubes. The vessel contains water and a few grammes of paraffin to prevent the evaporation of the former. It is heated until the water boils. The tubes are shaken now and then. The solution is completed when no more gas bubbles appear; about ¾ of an

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hour will be required. Sometimes a reddish-yellow deposit forms on the glass, which must be dissolved by shaking, or the solution must be filtered. The tubes are taken out of the hot water and put into a beaker of cold water. They must be covered to exclude daylight.

The burette for determining the carbon should have a capacity of 30 c. c. and be graduated to $\frac{1}{10}$ c. c., its diameter being about 12 mm. The solution is brought into the burette through a filter, if necessary, especially if the fluid is turbid. Then distilled water is added. The quantity of water, including that necessary for washing the tube, must be at least equal to the quantity of nitric acid used, and the total volume must not be less than 8 c. c., when it is to be compared with the standard solution.

The normal standard solution is prepared by dissolving standard steel. Thus, 0.1 gramme standard steel, containing 0.8 per cent. of carbon, is dissolved in 4 c. c. nitric acid and diluted to 8 c. c. Solutions of $\frac{1}{2}$, $\frac{1}{5}$, $\frac{1}{10}$, and $\frac{1}{20}$ the normal strength are also prepared. These standard solutions are marked and used as follows:

| | Percentage of Carbon per 1 c. c. for 0.1 gramme Iron. | To be used for Iron with a percentage of Carbon = |
|---|---|---|
| N | 0.10 | 0.8 and more. |
| $\frac{1}{2}$ N | 0.05 | 0.4 to 0.80. |
| $\frac{1}{5}$ N | 0.02 | 0.10 to 0.50. |
| $\frac{1}{10}$ N | 0.01 | 0.08 to 0.25. |
| $\frac{1}{20}$ N | 0.005 | 0.04 to 0.08. |

The solution in the burette, of the iron to be tested, is further diluted until the color corresponds to that of a standard solution. Multiplying the percentage of carbon in 1 c. c. of the standard, by the number of c. c. of the solution containing the iron to be tested, when the colors correspond, gives the percentage of carbon in the iron.

**Silicon.** — One to two grammes gray cast-iron, or three to four grammes white cast iron or wrought iron, are dissolved in 12 to 15 c. c. nitric acid (sp. gr. 1.2), to every one gramme iron, in a capacious beaker, the iron being added little by little to the acid. The solution is evaporated to dryness in a porcelain crucible and heated to redness; after cooling, 4 c. c. concentrated nitric and 6 c. c. concentrated hydrochloric acid (to one gramme iron) are added and the solution gently warmed till all ferric oxide is dissolved, diluted with an equal volume of water, warmed in a water-bath, filtered through a rather small filter, and washed with cold water. The filtrate is set aside for use in the determination of phosphorus. The filter is dried, placed in a platinum crucible, and heated to burn up all the carbon. The residue is mixed, in the crucible, with five times its mass of sodio-potassic carbonate, with addition of a little water, heated gently at first, then strongly till gas no longer escapes; the mass is allowed to cool, softened with water; evaporated to dryness after adding hydrochloric acid in a beaker to acid reaction, dissolved in water and filtered. The resulting silica is ignited and weighed. The amount of silicium may be computed from the weight of silica obtained.

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**Silicium in Steel.** — Ten grammes steel are dissolved in 140 c. c. of a mixture of sulphuric acid and water in the proportion of one part strong sulphuric acid to 6 of water. The liquid is boiled until all the steel is dissolved and then evaporated to dryness. The white salt is taken up with water and a few drops of hydrochloric acid, the silica filtered off, washed with hot water containing 5 per cent nitric acid, dried, ignited and weighed.

**Phosphorus.** — The solution for the determination of phosphorus, obtained in the determination of silicium, is condensed by evaporation to 20 c. c. for every one gramme iron. The phosphorus is then determined by the method already explained for the determination of phosphorus in iron ores.

**Phosphorus in Steel.** — Ten grammes steel are dissolved in a mixture of equal volumes of strong nitric (1.42) and hydrochloric (1.195) acids. The solution is evaporated to dryness and heated until all dark fumes have ceased to escape. A beaker or a porcelain dish may be used. The dry mass is then dissolved in strong hydrochloric acid, the excess of acid removed by evaporation, hot water added and the silica (unless present in minute quantity only) is filtered off, dried, ignited and weighed. The filtrate is evaporated down to a small bulk, so that it is only just liquid. It is allowed to cool, and then about 4 c. c. of the strong nitric acid are added. A little rinsing water is introduced so as to make the bulk about 20 c. c. The beaker is strongly shaken in the right hand, while from a pipette, which is held in the left hand, 20 c. c. of a solution of ammonium molybdate are allowed to run into the beaker in a thin stream.

The molybdate solution is prepared by dissolving 100 grammes ammonium molybdate in 1,000 c. c. water and 100 c. c. ammonia of sp. gr. 0.88.

After pouring in the molybdate solution, a few drops of ammonia (0.88) are added, and the beaker is shaken until the precipitate of iron has disappeared. The precipitate is allowed to settle in a warm place. After settling, the liquid is poured on a good Swedish 4-inch filter; the filter is washed with cold water containing one per cent. of nitric acid until it is quite white; the precipitate is washed in the beaker once by decanting with ordinary water, moderately hot; then it is washed down on the filter, and collected at the centre, with as few washings as possible, with ordinary water, moderately hot. The filter should be quite white before the precipitate is washed on to it.

After washing, the filter containing the precipitate is unfolded on another filter, and placed in a warm place (100° to 140° C.) to dry, covered with a large watch-glass to exclude dust. When dry the precipitate is shaken into a weighed platinum or porcelain dish as completely as possible, applying a brush to obtain the last particles, and weighed. Arsenic, if present, increases the weight of the precipitate.

**Sulphur.** — The method here given depends upon the degree of coloration of silver by the sulphuretted hydrogen evolved from decomposing iron sulphide.

*Apparatus and Reagents.* — 1. — A plate of silver, 15 mm. long, 6 mm. broad,

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1 mm. thick, composed of 75 parts silver and 25 parts copper, with a small hole at one corner for the attachment of a wire, for the purpose of suspending it vertically. It is very carefully cleaned, without being touched by the hand, by means of a scrubber covered with soft leather and strewed with fine sand powder. It is then cleaned with filter paper.

2. — A platinum wire ½ mm. in thickness, 40 mm. long, bent into S form for suspending the silver plate.

3. — A cylindrical bottle, with short, somewhat narrow neck, 23 mm. wide at widest, 120 mm. high up to neck, 15 mm. wide at neck. The neck is closed with a well-fitting cork, on the under side of which is attached a hook of platinum for the attachment of the silver plate.

4. — Sulphuric acid (sp. gr. 1.23).

*The Process.* — Finely-pulverized iron, 0.1 gramme, is placed in the bottle, 1.5 or 1.3 c. c. sulphuric acid is added, and the cork, to which the silver plate has been attached, is inserted as rapidly as possible. The plate should hang diagonally, 3 to 10 mm. below the cork. The bottle is carefully shaken, and the silver left for 15 minutes.

It is then removed and its color noted. If unaltered the iron is free from sulphur.

| | |
|---|---|
| Light-Yellow indicates | 0.01 per cent. S. |
| Brass-Yellow, | 0.02 " " |
| Golden-Yellow, | 0.03 " " |
| Tombac-Brown, | 0.04 " " |
| " " shading into blue, | 0.05 " " |
| " " shading more into blue, | 0.06 " " |
| " " with as much blue as brown, | 0.08 " " |
| Steel-Blue, with decided brown, | 0.10 " " |
| " " with trace of brown, | 0.15 " " |
| " " without brown, | 0.20 " " |
| Bluish gray, more than | 0.20 " " |

**Manganese.** — Of spiegel-eisen 0.5 gramme, of cast-iron 2 grammes, of wrought-iron 3 grammes, are dissolved in hydrochloric acid, with addition of nitric acid, and, if necessary to increase the percentage of iron, ferric chloride solution is added. The solution is treated as in the analysis of ores, using 1.3 to 2.3 grammes calcium carbonate as more or less iron is present, adding one gramme before the addition of the calcium hypochlorite solution.

**Manganese in Steel.** — *Bromine and Ammonia Process.* — Three grammes steel are dissolved in a litre flask by means of aqua-regia; the solution is boiled down and finally dried. The mass is dissolved in hydrochloric acid by boiling; water is added until the volume of liquid is 750 c. c., the solution is then neutralized with ammonia or ammonium carbonate. If too much ammonia is added, care must be taken immediately to add some hydrochloric acid, and to boil for a short time, so as to prevent the precipitation of manganese. When neutralization is completed, 20 to 30 c. c. of strongly concentrated, thick ammonium acetate are

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added, and the liquid is boiled until the precipitate settles clear, after lifting the flask from the lamp. If the supernatent liquid will not become clear a few drops of strong ammonia (0.88) are cautiously added, the flask is shaken and the liquid boiled for a moment again. Great care must be taken not to add too much ammonia, as the manganese may then be partly precipitated as hydrated oxide. After settling, the clear liquid is passed through a filter 10 inches in diameter, into a large flask; the precipitate of basic ferric acetate is then poured on the filter, and the remainder of the liquid allowed to filter well off. When no more drops seem to come from the funnel, the basic acetate is washed down into the first flask by means of boiling water, and hydrochloric acid is added. The flask is well shaken and heated to boiling, in order to insure the remainder of the manganese being present only as manganous oxide. Neutralization and precipitation are then repeated as before, and the filtrate added to the one first obtained. For steel, two precipitations are sufficient; but when much manganese is present more will be necessary. After every re-solution a good boiling is necessary.

The collected filtrates in the large flask are then allowed to cool, about 4 c. c. of bromine are added and the flask well shaken. It is best to add so much bromine as to produce quite a reddish color in the solution. Ammonia (0.88) is then added in excess, and the flask well shaken. After continued shaking the brown color becomes more and more evident and the oxide of manganese separates in lumps. The liquid is now boiled for a few minutes, allowed to settle, and then filtered off. The precipitate is washed with hot water, dried, ignited and weighed.

$$Mn\,(C_2\,H_3\,O_2)_2 + 5\,Br + (x+2)\,H_2\,O = (Mn\,O_2 + x\,H_2\,O) + 5\,NH_4\,Br + 2\,[\,NH_4\,(C_2\,H_3\,O_2)\,] + N.$$

| | Pig Iron. | | Wrought Iron. | Steel. |
|---|---|---|---|---|
| | Lake Superior Charcoal Iron. | Cleveland Ironstone, Clarence Furnaces. | Dannemora Soft Iron. | German Bessemer Steel. |
| Fe. | 93.34 | 93.59 | 99.471 | 98.544 |
| C, combined. | 0.38 | 0.85 | } 0.352 | } 0.046 |
| C, graphite. | 3.39 | 2.70 | | |
| Si. | 2.28 | 0.66 | 0.050 | 0.634 |
| S. | 0.03 | 0.35 | 0.027 | 0.045 |
| P. | 0.10 | 1.05 | 0.025 | 0.093 |
| Mn. | 0.17 | 0.79 | 0.075 | 0.638 |

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# SECTION 4.

## Fuels.

The term *Fuel* is applied to all substances that may be usefully employed for the production of heat by combustion with atmospheric air. Any substance susceptible of oxidation may be made to burn, but only those that ignite by a moderate preliminary heating, burn with comparative rapidity, and are obtainable in quantity at a moderate price, are ordinarily called fuels. The most important of the fuels are the hydrocarbon-compounds, composed of carbon, hydrogen, and oxygen, such as wood, coal, peat and their derivatives. They are all of vegetable origin, the proportions of the constituents vary greatly, and all contain more or less of mineral matter. Those which contain a large proportion of volatilisable combustible matter burn with flame, while the more purely carbonaceous fuels burn with but little. The amount of water in fuel varies from nothing to as much as 40 per cent; since this water is evaporated in the combustion, a certain amount of heat is lost thereby. The object of coking is to drive off this water and also volatilisable impurities, such as sulphur, thus increasing its heating power.

**Calorific Power.** — The calorific power of a substance is the amount of heat evolved during its combustion. The calorific power of ordinary hydro-carbon fuels may be approximately calculated from their known composition. Most of these fuels contain oxygen, and it is found that the heat developed by the perfect combustion of the fuel is equal to that due to the perfect combustion of all the carbon, and of so much of the hydrogen as is in excess of that required to form water with the oxygen present. The remainder of the hydrogen may be considered in union with the oxygen in the state of water. In estimating the heat evolved, there must be deducted that required to evaporate this water.

The calorific power of one kilogramme of hydrogen is 34462 C units of heat, that of one kilogramme carbon is 8080 C units of heat. The number 34462 was obtained by burning one kilogramme hydrogen, and in the process the water formed by this combustion was condensed, and therefore gave out its latent heat. In burning fuels by ordinary processes this water passes off as vapor; hence, the heat required to evaporate the water produced by the combustion must also be deducted. Hygroscopic moisture, if present, will be evaporated, and the heat required must also be deducted.

The calorific power is the same whether the body burns in air or in oxygen, it is also independent of the time involved, and is proportional to the weights of the substances burning.

*Problem* 1. — Required, the calorific power of one kilogramme wood, assuming its composition as $C_6 H_9 O_4$.

$$C_6 H_9 O_4 = C_6 H (H_2 O)_4 . \text{ Mol. Weight} = 145.$$



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In 145 kg. wood there are $\begin{cases} 72 \text{ kg. C,} \\ 1 \text{ " H,} \\ 72 \text{ " } H_2O. \end{cases}$

$H_2 + O = H_2O.$ $\qquad$ 2 : 18 :: 1 : 9.

In burning, 1 kg. H produces 9 kg. $H_2O$.

Total to be evaporated = 72 + 9 = 81 kg. $H_2O$.

| | | | |
|---|---|---|---|
| Units of heat due to burning of 72 kg. C | = 72 × 8080 | = | 581760 |
| Units of heat due to burning of 1 kg. H | = 1 × 34462 | = | 34462 |
| Units of heat due to burning, total, | | = | 616222 |
| Units of heat, latent, | = 81 × 540 | = | 43740 |
| Units of heat due to burning of 145 kg. wood, | | = | 572482 |

Hence, calorific power of one kg. wood is,

$$\frac{572482}{145} = 3948 \text{ C Units.}$$

*Problem* 2. — Given the average composition of air-dried wood,

| | |
|---|---|
| Carbon, | 400 |
| Hydrogen, | 48 |
| Oxygen, | 328 |
| Nitrogen and Ash, | 24 |
| Hygroscopic Moisture, | 200 |
| | 1000 |

Required the calorific power of one kilogramme.

The proportion of O to H in water is 16 : 2.

16 : 2 :: 328 : x = 41 grammes H combined with O.

48 — 41 = 7 grammes H which burn and produce heat.

1 gramme H produces 9 grammes water by combustion.

48 grammes H produce 48 × 9 = 432 grammes water.
200 grammes water, hygroscopic.
632 grammes water, total.

| | | | |
|---|---|---|---|
| 400 grammes C yield | 400 × 8.080 | = | 3232 Units of Heat. |
| 7 grammes H yield | 7 × 34.462 | = | 241 " " " |
| | | | 3473 " " " |
| Heat required to evaporate 632 grm. water, | 632 × 540 | = | 341 |
| Calorific power of one kg. wood . | | = | 3132 |

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A unit of heat is equal to 423 kilogramme-metres of work; hence, the units of work corresponding to the calorific power of one kilogramme wood is equal to $3132 \times 423 = 1{,}324{,}836$. In the steam-engine heat of combustion is converted into work, but only about one-twentieth of the power of the fuel can be utilized: to find a more economical means of utilizing this power is one of the great problems of the present age.

The calorific power of a fuel may also be determined by ascertaining the weight of fuel required to evaporate a given weight of water at a known temperature. The number of units of heat required for this purpose are known, since one unit of heat will raise the temperature of a kilogramme of water one degree centigrade. This is practically true up to the boiling point, 100° C, at which temperature the water evaporates, and it is also known that every kilogramme requires 540 units of heat for its evaporation.

*Problem.* — It has been ascertained by experiment that one kilogramme of coal will evaporate 9.17 kilogrammes of water at 88° C, what is the calorific power of the coal? $100 - 88 = 12$.

$$(12 + 540) \times 9.17 = 5061.84 \text{ Units of Heat.}$$

This was the method used by Professor W. R. Johnson, of Philadelphia, in his elaborate Report of Experiments on the evaporating power of American coals, made to the Secretary of the Navy in 1843–4. Similar experiments were made by the Quartermaster-General, General M. C. Meigs, in Washington, in the years 1879, 1880, 1881, and 1882, for the purpose of determining the proper issue of different varieties of coal to the Army, by determining their relative evaporating powers. The apparatus used in these experiments is an upright tubular steam boiler.

The calorific power of a fuel, as determined by experiment, is generally less than that calculated from its chemical composition, in consequence of the absorption of a certain amount of heat attending the chemical decomposition of the fuel.

The calorific power of fuel is of importance in some of its practical applications, such as the heating of steam-boilers, the warming of buildings etc.

**Calorific Intensity.** — The calorific intensity of a fuel is the maximum temperature developed in its combustion, and, assuming that all the heat is retained by the products of combustion, it may be defined as the temperature to which the heat generated by the burning of each portion of the fuel, can raise the products of its own combustion. There is no trustworthy experimental method for determining calorific intensity, it is therefore obtained by calculation from the calorific power.

Assuming that the calorific power of a fuel is C, that the weights of the various products of combustion are W, W′, W″, etc., and that the specific heats of these products are, respectively, S, S′, S″, etc., then $WS + W'S' + W''S'' + \text{etc.}$,

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represents the amount of heat required to raise the temperature of the whole mass of the products one degree centigrade, and the maximum temperature to which these products can be raised in the process of combustion must be

$$T = \frac{C}{W S + W' S' + W'' S''}$$

The numerator represents the total number of units of heat produced in the combustion, the denominator represents the number of units of heat required to raise the temperature of the products one degree, the quotient must therefore represent the total number of degrees through which the temperature of the products is raised.

The calorific intensity is independent of the weight of the substance consumed, but is dependent upon the time and upon the atmosphere in which the combustion takes place, being greatest in pure oxygen.

*Problem.* — The average composition of air-dried wood being

| | |
|---|---|
| Carbon, | 400 |
| Hydrogen, | 48 |
| Oxygen, | 328 |
| Nitrogen and Ash, | 24 |
| Hygroscopic Moisture, | 200 |
| | 1000 |

required its calorific intensity, burned in oxygen and in air.

Let it be assumed that the quantity of fuel burned is one kilogramme.

Now, as determined under calorific power, .041 kilogrammes of H are already combined with O, leaving but .007 for combustion.

In combustion, $C + 2\,O = CO_2$. Or, 12 parts C + 32 parts O produce 44 parts $CO_2$.

Also, $2\,H + O = H_2O$. Or, 2 parts H + 16 parts O produce 18 parts $H_2O$.

Hence, 12 : 44 :: .4 : x = 1.467 kg. $CO_2$ produced in the combustion of the carbon.

And, 2 : 18 :: .007 : y = 0.063 kg. $H_2O$ produced in the combustion of the available hydrogen.

And, 2 : 18 :: .041 : z = 0.369 $H_2O$ already existing in the wood, and evaporated by the heat.

Hygroscopic moisture, 0.200. Total steam produced, 0.632.

Specific heat of $CO_2$ = .22

Specific heat of $H_2O$ (steam) =. 50

$$T = \frac{3132}{1.467 \times .22 + 0.632 \times .50} = 4903°\ C, \text{ in Oxygen.}$$

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In case the combustion takes place in air, a certain amount of nitrogen will be heated and thus reduce the maximum temperature. The average composition of air, by weight, in 100 parts, is

| | |
|---|---|
| Oxygen, | 23 |
| Nitrogen, | 77 |
| | 100 |

$$C + 2\,O = CO_2.$$

$12 : 32 :: .4 : x' = 1.067$ parts O required by the Carbon.

$$2\,H + O = H_2O.$$

$2 : 16 :: .007 : y' = 0.056$ parts O required by the Hydrogen.

$1.123$ parts O required by the wood.

$23 : 77 :: 1.123 : z' = 3.759$ parts N introduced.

Specific Heat of N = .25.

$$T = \frac{3132}{1.467 \times .22 + 0.632 \times .50 + 3.759 \times .25} = 1984°\ C,\ \text{in Air.}$$

The actual calorific intensity is always lower than that obtained by calculation, because the combustion is either incomplete, part of the carbon burning only to CO, or else, an excess of air is introduced, which takes up the heat: portions of the carbon and hydrogen are also volatilized by the heat without being burned, and the products of combustion never completely retain all their heat. Nevertheless, the calculations furnish good comparative results, and are useful in determining the particular fuel to be used in metallurgical operations, where high temperature is the main requisite.

*Analysis of Fuel.*

In the analysis of fuel, a preliminary examination is made to determine the form and size of the fragments, their hardness, etc., and to note the presence of admixtures. Several kilogrammes, of the size of an egg in case of coal, are thrown into a furnace in which a fire is kindled, and the effect noted. Whether it kindles easily or with difficulty, whether the flame deposits soot, whether it burns with a quiet or crackling flame, whether the flame is long or short, whether it burns without odor, etc.

The specific gravity is determined by one of the methods given under that subject, and best by using alcohol as the liquid for immersion.

The sample for analysis is selected with the usual precautions.

**Moisture.** — For ordinary purposes 2 to 4 grammes of the pulverized substance are heated between watch-glasses for two hours, in an air-bath, at 100° C. The watch-glasses containing the substance are then rapidly transferred to a desiccator and allowed to cool. The weight is taken and the loss noted as moisture.

**Volatile Matter and Coke.** — A weighed quantity of the substance, about one gramme, in course powder, is placed in a platinum crucible, fitted loosely with



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a lid, and heated to a red heat until the flame of the escaping gas is no longer visible; the temperature is then raised to a white heat and retained for five minutes. The crucible is then transferred to a dessicator, allowed to cool, and weighed. The loss of weight, less the moisture, is the volatile matter. The weight of the residue is the amount of coke obtainable from the coal.

**Ash.** — From 3 to 5 grammes of the substance, in course powder, are placed in a platinum crucible and heated, preferably in a muffle, until all combustible matter is consumed. To determine whether any carbon remains, alcohol is added, and the contents are stirred, when particles of carbon, if present, become visible. The heating is then continued to burn off the alcohol, as well as the remaining carbon. The crucible is allowed to cool and is then weighed, the weight of the residue determines the ash. Its color is noted.

**Sulphur.** — This element exists in coal principally in two forms, one combined with calcium as sulphate or sulphide, the other combined with iron as pyrite. The former is perfectly harmless, while the pyrite seriously affects the quality of the iron, in the manufacture of which the coal is used. The former remains in the ash, while the latter largely passes into the products of combustion.

About 5 grammes of coal, finely divided, are boiled in water with an equal weight of sodium carbonate for 20 hours, by which means the calcium sulphate is decomposed, while the iron sulphide remains unattacked. The residue is then filtered, and rapidly washed with boiling water. In the case of coke, nitric acid in slight excess must be added to the filtrate to convert sodium sulphide into sulphate. The sulphuric acid in the *filtrate* is then determined in the usual way, by adding barium chloride, filtering, igniting the precipitate, and weighing. From the weight of the barium sulphate thus obtained the amount of sulphur is calculated, and represents that present in combination with calcium.

To the *residue*, nitric acid is added, the liquid is concentrated by evaporation, sodium carbonate added in excess, and the whole heated to near the fusing-point, by which means the iron, silica and alumina are rendered insoluble. The mass is then treated with water, well washed, and the filtrate acidified with acetic acid; barium chloride is then added, the solution filtered, and the precipitate dried, ignited and weighed. The sulphur thus found represents that present as pyrite in the coal.

To determine the *total sulphur*, one gramme finely pulverized coal is intimately mixed with 1½ times its weight of an intimate mixture of 2 parts calcined magnesia and one part sodium carbonate free from moisture, and heated in an uncovered platinum crucible, placed in an inclined position, so that only the lower half becomes ignited. The mass is frequently stirred with a platinum wire. The fusion requires about one hour and its completion is indicated by a change in color from gray to yellow or red. The mass is then covered with hot water, and bromine water is added until the liquid is pale yellow; it is then boiled, decanted through a filter,

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and washed with hot water. The filtrate is acidified with hydrochloric acid, boiled until it becomes colorless, and the sulphuric acid precipitated with barium chloride, as before.

In order to determine the amount of *sulphur which passes into the products of combustion*, the combustion-process must be used. For this purpose, one gramme pulverized coal, in a platinum combustion-boat *b*, *Fig.* 1, *Pl. VI*, is placed in the combustion tube, and the latter is heated while a stream of oxygen is transmitted through it. The products pass through the absorption tube *c*, containing hydrochloric acid and bromine. The sulphuric acid formed is precipitated with barium chloride as before.

**Phosphorus.** — The determination of this element in coal has acquired great importance on account of the enormous increase in the production of steel in late years, this element being carefully excluded from the iron used in the manufacture of the steel.

The *ash* of the coal is first determined.

Sufficient coal is then burnt to yield two grammes of ash, preferably on platinum foil in a muffle. When the combustion is completed, the warm ash is poured into a weighing tube, *Fig.* 7, *Pl. I*, the end of which is then closed. When cold it is weighed, the required quantity poured out into a porcelain dish, and the tube again weighed, the loss of weight is the weight of the quantity used. This is then digested for some time with strong hydrochloric acid on the water-bath, and finally evaporated to dryness. The residue is moistened with hydrochloric acid, and, after standing for some time, 100 to 150 c. c. cold water are added. It is then heated on the water-bath, allowed to cool and filtered into a second dish. The acid solution is evaporated, with frequent addition of nitric acid, nearly to dryness, taken up with water containing a little nitric acid, and washed into a beaker. The solution is decomposed by means of a large excess of a solution of nitric acid and ammonium molybdate, heated for several hours to 50° or 60° C; the yellow precipitate is brought upon a small filter, and washed with a solution of two parts ammonium nitrate in 20 parts water and one part nitric acid, until the washings are scarcely colored by potassium ferrocyanide. The funnel is placed on a small beaker, and the yellow precipitate is dissolved, with the aid of a feather, by means of ammonia. The latter is first poured into the vessel, in which the precipitation took place, in order to dissolve any remaining particles of precipitate. The ammoniacal solution is decomposed by addition of hydrochloric acid, drop by drop, until the resulting precipitate begins to disappear but slowly upon shaking the solution. A mixture of 110 parts crystallized magnesium chloride, 140 parts ammonium chloride, 300 parts ammonia (0.91) and 700 parts water, in not too great excess, is then added.

The solution is allowed to stand for at least 12 hours. The precipitate is then transferred, by means of the supernatent liquid itself, to a filter, and washed with very small quantities of dilute ammonia (1 : 3), till acidified silver nitrate solution

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produces but a slight opalescence in the washings. The precipitate, while still moist, is transferred to a weighed platinum crucible and very slowly heated; the burning of the filter being completed by half covering the crucible with its lid. In case the pyrophosphate is not white, it is moistened with nitric acid, gently evaporated, and the mass once more ignited. The amount of phosphorus is computed from the weight of the magnesium pyrophosphate, $Mg_2 P_2 O_7$, thus obtained.

**Carbon and Hydrogen.** — These elements are determined by combustion in oxygen. The combustion tube (85 c. m. long), *Fig.* 2, *Pl. VI*, contains two asbestus stoppers, *a*, wrapped in very thin platinum foil, and between these is placed a layer of granular cupric oxide. The tube is placed in the trough O of the furnace, *Fig.* 3, *Pl. VI*, the tiles are placed in position over it, and the cupric oxide layer is heated by means of the burners B to a red heat. For ten minutes a stream of air, first passing through caustic potash and concentrated sulphuric acid, is conducted through the tube, which is finally allowed to cool in this current. The stopper *u* is removed, and the coal, about 300 m. g., (which has been dried at 100° C. out of contact with air), contained in the platinum boat *m* is inserted, and the stopper replaced; at the other end the U tube, containing spongy calcium chloride is attached, and to this is attached a smaller U tube, containing glass beads moistened with a few drops of sulphuric acid. These U tubes are weighed together before being attached. To the smaller U tube is attached a Liebig caustic potash apparatus, *Fig.* 7, *Pl. V*, containing a solution of caustic potash of 1.3 to 1.35 specific gravity, and having a U tube, like that of the calcium chloride tube, attached at the end *f*. The caustic potash apparatus is weighed together with this U tube. Finally, a straight, unweighed calcium chloride tube is attached, to prevent access of moisture from the aspirator.

The cupric oxide layer is heated to redness by the burners B, a current of oxygen, previously passed through caustic potash and concentrated sulphuric acid, is then slowly transmitted through the tube, and the platinum boat heated by means of the burner A, beginning at the rear end and passing gradually forward, until all combustible matter is consumed. The oxygen is cut off, and purified air transmitted as before. In a few minutes the calcium chloride and the potash apparatus are removed and weighed. Meanwhile, the gas is turned off, and the tube allowed to cool in the current of air. The platinum dish is weighed to determine the ash. The cupric oxide layer can be used for 30 combustions.

The increase in weight of the calcium chloride apparatus gives the weight of the water produced by the combustion, from which the hydrogen can be computed. Thus, if this increase is 107 m. g., then,

$$H_2 O = H_2 + O.$$

$$18 : 2 :: 107 : x = 11.89 \text{ m. g. hydrogen in 300 m. g. coal.}$$

$$300 : 11.89 :: 100 : y = 3.96 \text{ per cent H.}$$

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The increase in weight of the caustic potash apparatus determines the weight of carbon dioxide produced in the combustion, from which the carbon can be computed. Thus, if this increase is 829 m. g., then,

$$CO_2 = C + 2\ O.$$

$$44 : 12 :: 829 : x' = 226.1 \text{ m. g. carbon in } 300 \text{ m. g. coal.}$$

$$300 : 226.1 :: 100 : y' = 75.37 \text{ per cent. C.}$$

There is no reliable method for determining directly the amount of oxygen in organic substances, hence it is generally determined by difference.

**Gas.** — To determine the value of a fuel for gas-making purposes, 5 grammes are heated, as rapidly as possible, in a retort, the gas being passed through solutions of lime water and lead acetate, and collected over mercury in a graduated glass cylinder. A coal containing much sulphur is unfit for making gas.

**The Weather-Waste of Coal.** — It is known that coal deteriorates by exposure to the weather, by absorption of oxygen and consequent oxidation of part of the carbon and hydrogen. It has been stated that coal exposed for nine months loses 50 per cent. of its value as fuel (Grundman). According to the experiments of the German Railway Association, and of the Geological Survey of Pennsylvania, compact coals do not change materially in their chemical composition, by exposure for several months. But according to the recent experiments of Richters, weathering diminishes the heating power, and the capacity to yield gas.

*Coal Analyses.*

| | Pennsylvania Colliery. Bituminous. | Fairmount Coal. Bituminous. | Logan Colliery. Bituminous. | Connalsville Coal, used for foundry Coke. | Stone's Gas Coal. Penn'a. | Lignite. Texas. | Lehigh. | Lackawanna. |
|---|---|---|---|---|---|---|---|---|
| Water | 0.810 | 1.370 | 0.620 | 4.50 | 3.00 | 11.00 | 0.000 | 2.120 |
| Volatile Matter. | 20.640 | 37.680 | 22.135 | 24.00 | 34.00 | 39.50 | 5.285 | 3.793 |
| Fixed carbon(by dif | 74.023 | 39.353 | 68.728 | 65.00 | 58.00 | 45.00 | 89.153 | 87.741 |
| Sulphur. | 0.507 | 8.427 | 0.867 | | | | | (0.123) |
| Ash. | 4.020 | 13.170 | 7.650 | 6.50 | 5.00 | 4.50 | 5.562 | 6.346 |
| | 100.000 | 100.000 | 100.000 | 100.00 | 100.00 | 100.00 | 100.000 | 100.000 |
| $P_2O_5$ | 0.007 | | 0.237 | | | | | |
| Coke. | | | | 71.50 | 63.00 | 49.50 | 94.715 | 94.087 |
| Lbs. of steam produced from water at 100° C. by 1 lb. fuel. | | | | | | | 8.930 | 9.790 |

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# SECTION 5.

## Potable Water.

A good drinking water is usually clear, limpid, without taste or odor, holding in solution carbon dioxide, air richer in oxygen than atmospheric air, and a little calcium carbonate. The smaller the quantity of organic matter it contains the better.

The impurities in water may be of two kinds, — specific poisons, as when it has received the excreta of a patient suffering from cholera or from typhoid fever, or abnormal quantities of impurities, organic or mineral. The most important impurity in water intended for drinking purposes is dissolved organic matter. Its effects seem to depend not so much on the amount as on the nature of the organic matter, its existence in certain conditions or its capability of promoting the development of organic germs. The whole subject of the influence of organic matter on the character of a water is involved in much obscurity, nevertheless there appears to be a connection between the prevalence of epidemic disease and the contamination of water used for domestic purposes with sewage or some similar impurity. The utility of all attempts to estimate organic matter depends upon the effect of variations of mere quantity of organic matter, which effect is very doubtful within the limits occurring in drinking water. The effect of dangerous waters is generally attributed to certain germs; but, as these organisms subsist on organic matter, the larger proportion of the latter furnishes more material for their development and may therefore be in some sort a measure of their abundance.

In order to form an opinion as to the character of a drinking water, it is necessary to ascertain the following data: —

Total solids at 100° C.
Chlorine.
Free and albuminoid ammonia.
Oxygen consumed in oxidising the organic matter.
Nitrogen as nitrites and nitrates.
Nitrous acid.
Poisonous metals.

In particular cases it may be necessary to determine also

Hardness.
Sulphates.

**Collection of Sample.** — Whenever possible, at least half a gallon of the water to be examined should be obtained in quart bottles with glass stoppers. Great care must be taken to have the bottles perfectly clean and nearly full of the water. It should be kept in a cool dark place until examined, which should take place within forty-eight hours after collection. Samples should also be set aside in half-filled but closed glass-stoppered bottles for 10 or 12 days, and one of these examined every day or two, so as to trace the character and extent of the changes undergone.

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In collecting water from a main it should be allowed to run in order to clear the pipe. In collecting from a river, or pond scum should be avoided and the sample should be collected towards the middle in order to obtain an average sample; a note should be made to that effect if there has been heavy rain or long drought.

The following facts are also ascertained and noted: — The nature of the source of the water, spring, well, river, etc., the depth in case of a well, the geology of the district, the character of the soil and subsoil, and the distance from the source of water of the nearest filth or drain.

**Preliminary Examination.** — The physical properties of the water are first noted. The color is observed by filling a Nessler glass of 50 c. c. capacity and looking through it on a porcelain tile, using for comparison a similar glass filled with pure water The taste and odor are determined, both when the water is cold and when it is slightly warmed. The presence of suspended matter and minute vegetable or animal organisms is noted. The reaction of the water to test-paper is also determined.

**Solid Residue at 100° C.** — A platinum dish of 100 c. c. capacity is cleaned, put into hot water, wiped and allowed to cool in contact with a slab of porcelain. It is then weighed and placed over a water bath, *Fig.* 4, *Pl. VI*, consisting of a beaker containing boiling distilled water; a small piece of filter-paper is inserted between the dish and the beaker to allow the escape of steam. One hundred c. c. of the water to be examined are poured into the platinum dish and evaporated to dryness; the dish is removed, wiped externally, allowed to cool in contact with the porcelain slab, and weighed. The increase in weight is the solid residue, it is multiplied by 10.000 and recorded as parts per million. In case the weight increases rapidly during the process of weighing there are deliquescent salts present and the weight must be taken as rapidly as possible. A few drops of hydrochloric acid are now added to the residue, effervescence proves the presence of carbonates. The residue is finally ignited, deflagration indicates the presence of nitrates; organic matter is indicated by the blackening of the residue. The solid residue consists principally of saline matter. A potable water should not contain over 400 to 500 parts per million. The determination of the total solids is important as furnishing a check on the other quantitative determinations.

**Chlorine.** — Chlorine occurs in drinking water combined usually with sodium, sometimes with calcium, potassium, and magnesium. Unless excessive it is harmless in itself, but as urine and sewage are comparatively highly charged with chlorides, its presence is an indication of sewage contamination, especially when the amount is above that of the average waters of the district, and which has been derived from the soil. The evidence afforded by the test for chlorine is taken in connection with the organic matter, much chlorine associated with an excess of free and albuminoid ammonia being a strong indication of sewage contamination. The absence of chlo-

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rine, or its presence in small quantity, is an indication that there has been no animal or sewage contamination, but there may still be vegetable contamination.

A standard solution of silver nitrate is prepared by dissolving 4.79 grammes of the crystallized salt in one litre of distilled water. One c. c. of the solution will precipitate one milligramme of chlorine.

$$Ag\ NO_3 + Na\ Cl = Ag\ Cl + Na\ NO_3.$$

$$170 : 35.5 :: \tfrac{4.79}{1000} : x = .001 \text{ gramme.}$$

One hundred c. c. of the water to be examined are placed in a clean porcelain dish, about 30 milligrammes of potassium chromate, pure, are added and the water is stirred until the salt is dissolved, coloring the water distinctly yellow. The standard solution of silver nitrate is carefully added from a pipette graduated to $\frac{1}{10}$ c. c., the water being continually stirred, until the red color just begins to be permanent; the amount of silver nitrate solution used is noted. The number of grammes of chlorine corresponding, multiplied by 10,000, gives the parts per million. If either the water or the silver nitrate solution is acid, it is first neutralized with caustic potash.

**Organic Matter.** — The determination of the organic matter is not only the most important process of the water analysis but also the most difficult. There are three principal methods in use, Frankland's "Combustion Process," which is omitted here, as it requires complicated and expensive apparatus and considerable experience; Wanklyn's "Albuminoid-Ammonia Process," and Tidy's "Permanganate Process." It is not possible to decide *absolutely* upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of these processes. In all cases the source and history of the water should be known, and other evidence should be taken in connection with the amount of organic matter. Standards of purity giving exact amounts of ammonia, albuminoid ammonia, or oxygen consumed, permissible or not, are only useful when they are merely *local*, applying to a particular water.

*Albuminoid-Ammonia Process.* — This process depends upon the fact, that when water is evaporated the putrescent organic matter it may contain is liable to decompose and give off its nitrogen in the form of ammonia. The measurement consists in determining first the free ammonia, partly probably derived from previous decomposition of organic matter, by distillation, and secondly in destroying the organic matter present by means of potassium permanganate and caustic potash, and estimating its amount by the amount of ammonia produced called albuminoid ammonia.

The following solutions are prepared.

*Nessler Reagent.* — By heating and stirring 35 grammes potassium iodide and 13 grammes corrosive sublimate are dissolved in 800 c. c. water, a cold saturated solution of corrosive sublimate added until the red color produced by the mercuric

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iodide just begins to be permanent. One hundred and sixty grammes solid caustic potash (or 120 grammes caustic soda) are added, and the liquid is diluted with water to bring the whole to one litre. A little more cold saturated solution of corroeive sublimate is added and the liquid allowed to settle. It is best to purchase this solution ready made. It must be kept in a well-stoppered bottle.

*Standard Solutions of Ammonia.* — Two solutions should be kept, a strong and a dilute. The strong solution is prepared by dissolving 3.15 grammes ammonium chloride in one litre of water. The dilute solution is prepared by taking 5 c. c. of the strong solution and diluting to ½ litre.

One molecule $NH_3$ . H Cl contains one molecule $NH_3$.

$$53.5 : 17 :: 1 : x = 3.15.$$

Hence, 1 c. c. of the strong solution contains 1 milligramme ammonia.
1 c. c. of the dilute solution contains $\frac{1}{100}$ milligramme ammonia.

*Solution of Potassium Permanganate and Caustic Potash.* — Two hundred grms. solid caustic potash and 8 grammes crystallized potassium permanganate are dissolved in one litre water, the solution is boiled until about one-fourth is evaporated and the loss is replaced by diluting to one litre. Each analysis requires 50 c. c., containing 10 grammes caustic potash and 0.4 gramme potassium permanganate.

The apparatus necessary for the performance of the process is represented in *Fig.* 5, *Pl. VI.* Great care must be taken in the cleaning and washing of the apparatus, always dashing a little distilled water on a piece of apparatus before using it.

The retort (capacity a little more than ½ litre) is washed out with good tap-water and mounted in its holder; the Liebig condenser is washed out with a little distilled water; the retort and condenser are then connected by means of an adapter, packing with paper to make the junction secure. Five hundred c. c. of the water to be examined are poured into the retort by means of a funnel, and the stopper, after dashing distilled water over it, is replaced. The water is distilled over and collected in a Nessler glass. When 50 c. c. have collected the Nessler cylinder is replaced by another. As the distillation proceeds the 50 c. c. of distillate are Nesslerized. Two c. c. of Nessler reagent are dropped into it by means of a pipette and the liquid is stirred with the pipette. If ammonia is present a yellow coloration results, and the more ammonia the deeper the color. The amount of ammonia present is determined by imitating this color with the standard dilute solution of ammonia. Fifty c. c. of distilled water are placed in a Nessler glass and more or less of the ammonia solution added for a burette; then two c. c. of the Nessler reagent are added, and allowed to act for three minutes. If the tint is too light more ammonia solution is added, if too dark another solution is prepared with less ammonia solution, until an exact imitation is obtained. The colors are best compared on a porcelain tile.



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The second, third and fourth distillates of 50 c. c. each are usually thrown away, ½ being added to the result of the first estimation for the total free ammonia. It is better, however, to Nesslerize each distillate, and in reporting the results the details of the evolution of the ammonia, as obtained in the separate distillates, should always be given. The process is usually stopped after the fourth distillate but it is better to continue the distillation until the last 50 c. c. contain less than one per cent. of the total ammonia already collected. The addition of ammonia-free water to the contents of the retort may be necessary in this case. Multiplying the total number of c. c. of ammonia solution required by two gives the milligrammes of ammonia per litre or parts per million.

About 300 c. c. are left in the retort, to which 50 c. c. of the solution of potassium permanganate and caustic potash are added and the distillation continued. The retort is gently shaken in case of bumping, giving the contents a waving motion. Usually three distillates of 50 c. c. each are collected and Nesslerized, but it is better to continue the distillation until the last 50 c. c. contain less than one per cent. of the total ammonia already collected. The apparatus is now allowed to cool after loosening the connection between the retort and condenser. Multiplying the total number of c. c. of ammonia solution required by two gives the milligrammes of ammonia per litre or parts per million. In reporting the results the details of the evolution of the ammonia, as obtained in the separate distillates, should always be given.

A separate distillation is made to determine *total ammonia* by adding the alkaline permanganate at once (before determining free ammonia). The results of the two, separate distillations are then compared.

From 0.0 to 0.05 albuminoid ammonia, in spite of much free ammonia and chlorides would pass a water as organically pure. Much free ammonia, over 0.08 per million, is an indication of contamination with urine in a recent condition, — the excess of chlorides will confirm this conclusion. Much albuminoid ammonia, over 0.10 per million, little free ammonia and almost entire absence of chlorides is indicative of vegetable contamination; such water is very injurious to health producing diarrhœa, etc. Much free ammonia and *over* 0.05 albuminoid ammonia is a suspicious sign. Albuminoid ammonia over 0.15 ought to condemn a water absolutely. (Wanklyn). No opinion should be founded solely on the results of this process for in that case rain-water in country places would sometimes be condemned as it contains 0.49 of free ammonia.

The value of the results by this process depends more upon the rate and progress of the evolution of ammonia than upon its total amount. The gradual evolution of albuminoid ammonia indicates the presence of organic matter in a comparatively fresh condition, while rapid evolution indicates that the organic matter is in a state of decomposition.

Some late improvements of the method have been suggested by Mr. Haines of

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Philadelphia. The retort should have a narrow neck, which can easily be thrust within the tube of the Liebig condenser for some six inches, the retort and condenser are connected by means of a short piece of rubber tubing tied down to both. The apparatus is cleaned by flushing the whole with tap-water through the tubulure of the retort several times. The water is removed from the retort by means of a glass syphon. To prepare permanganate solution free from ammonia, the caustic potash and the permanganate solutions are prepared separately, when cool the potash solution is poured into the permanganate solution and diluted to 1500 c. c., boiled down rapidly to 500 c. c., diluted to 1200 c. c., boiled again to 900 c. c. and when cool diluted to one litre. (*Journal Franklin Inst. Nov.* 1882).

*Permanganate Process.* — This process consists in estimating the amount of organic matter present in drinking water by the amount of oxygen required to oxidise it. Potassium permanganate is the oxidising agent used. If we represent the organic matter by oxalic acid the following is the reaction.

$$5\,(C_2\,H_2\,O_4\,.\,2\,H_2\,O) + 2\,Mn\,O_4\,K + 3\,H_2SO_4 = 10\,CO_2 + K_2\,SO_4 + 2\,Mn\,SO_4 + 18\,H_2\,O.$$

Hence, $2\,Mn\,O_4\,K$ yields 5 O.

$$316.2 : 80 :: x : 1. \qquad x = 3.9525.$$

A standard solution of potassium permanganate is prepared by dissolving 0.39525 gramme of the crystallized salt in one litre water. One c. c. of the solution yields .0001 gramme oxygen.

Two hundred and fifty c. c. of distilled water free from ammonia are placed in a flask and a like amount of the water to be examined in a similar flask. By means of a pipette 10 c. c. of sulphuric acid (one part acid mixed with three parts water) are added to each flask and the same quantity of the standard permanganate. The flasks are allowed to stand for three hours. A little solution of potassium iodide (one part potassium iodide in ten parts water is then added, taking care to have an excess, which is indicated by the disappearance of the pink color. The excess of potassium permanganate present in the contents of the flasks oxidises part of the iodide to iodate.

$$KI + 2\,K\,Mn\,O_4 = KIO_3 + K_2\,O + 2\,Mn\,O_2.$$

The sulphuric acid present decomposes the iodate in presence of iodide liberating iodine which colors the solution.

A standard solution of sodium hyposulphite (properly thiosulphate, $Na_2\,S_2\,O_3$), prepared by dissolving one gramme of the pure crystallized salt in a litre of water, is slowly added from a burette to the contents of each flask until the amber color nearly disappears.

$$2\,Na_2\,S_2\,O_3 + 2\,I = 2\,Na\,I + Na_2\,S_4\,O_6$$

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Before the color quite disappears two or three drops of starch solution, prepared by pouring on flour paste 100 times is weight of boiling water and allowing to settle, are added to each flask, and the addition of sodium hyposulphite is continued until the blue color entirely disappears. A single drop of the potassium permanganate solution should now color the entire solution in each flask pink.

To compute the results, 10 c. c. of permanganate were taken, equivalent to .001 gramme oxygen, and if A c. c. of hyposulphite were required for the pure water, then, $\frac{.001}{A}$ is the value in oxygen of one c. c. hyposulphite. Let B represent the number of c. c. of hyposulphite required for the water under examination, then,

$$\text{Total oxygen in permanganate used} = \frac{A \times .001}{A}$$

$$\text{Oxygen of permanganate remaining in excess} = \frac{B \times .001}{A}$$

$$\text{Oxygen consumed by organic matter} = \frac{(A - B)\ .001}{A}$$

This is the amount of oxygen consumed by the organic matter in ½ litre of the water examined, multiplying by four gives the amount per litre, which is recorded in milligrammes or parts per million.

The amount of oxygen consumed in this process is probably in all ordinary cases much below that required for complete oxidation of the organic matter present. This process gives better information by noting the rate and progress of oxidation than by determining the amount consumed in any given time. Therefore determinations should be made by allowing samples, after the addition of the permanganate, to stand 1, 3, 6, 9, 12, and 24 hours, then testing with hyposulphite as before. If at any time the pink tint disappears another 10 c. c. of permanganate is added. The temperature should be kept constant at 20° C, and the test bottles or flasks should be kept in the dark during the action of the permanganate. The solutions of sodium hyposulphite, potassium iodide and starch will not keep, but must be prepared fresh for every operation.

*Moist Combustion Process.* — The latest process for determining the amount of organic matter in drinking water is Wanklyn's "Moist Combustion Process." It consists in ascertaining the amount of oxygen required for the complete oxidation of the organic matter, and is a modification of the permanganate process.

Four solutions are prepared.

1. Solution of potassium permanganate, strength, one c. c. containing one mg. active oxygen.

$$10\ (Fe\ O\ .\ SO_3) + 2\ K\ Mn\ O_4 + 8\ H_2\ SO_4 = 5\ (Fe_2\ O_3\ .\ 3\ SO_3) + K_2\ SO_4 + 2\ Mn\ SO_4.$$

We see that 2 K Mn $O_4$ (mol. wt. 316.2) oxidises 10 Fe O to 5 $Fe_2$ $O_3$ and there-

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fore furnishes 5 O (at. wt. 80); hence, to furnish one part of oxygen will require $\frac{316 \cdot 2}{80} = 3.95$ parts K Mn $O_4$. The solution is prepared by dissolving 3.95 grammes permanganate in one litre water.

2. Solution of ferrous sulphate, strength, one c. c. absorbing one mg. active oxygen. From the equation above it is evident that 10 Fe $SO_4$ absorb 5 O, or, 1520 parts ferrous sulphate absorb 80 parts oxygen; hence, to absorb one part of oxygen will require $\frac{1520}{80} = 19$ parts anhydrous ferrous sulphate. Crystallized green vitriol contains Fe $SO_4$ . 7 $H_2$ O, therefore, 152 : 278 :: 19 : x = 34.73 parts green vitriol required to furnish 19 parts Fe $SO_4$. The solution is prepared by dissolving 34.73 grammes green vitriol in one litre water.

3. Solution of caustic potash.

4. Solution of sulphuric acid, containing one part acid to ten parts water.

One litre of the water to be examined is placed in a flask and 5 c. c. of the solution of caustic potash are added then 5 c. c. of the solution of permanganate. The flask is heated and about 900 c. c. are distilled over. The liquid remaining should retain a pink color. (In analyzing very bad waters it may be necessary to add another 5 c. c.). Ten c. c. of the solution of sulphuric acid are dropped into the retort and shaken up with the contents. Then 5 c. c. of the iron solution are added, and in a few minutes the liquid will become colorless. The solution of permanganate is now added from a graduated pipette till the red color just begins to be permanent. The total amount of permanganate used is noted. Subtracting the amount of permanganate used up by the iron solution (one c. c. iron solution requiring one c. c. permanganate solution), we obtain the number of milligrammes of active oxygen consumed by the organic matter in one litre of the water.

Water of first-class purity does not consume more than 0.50 mg. oxygen per litre, average drinking water 2.00 and 3.00; dirty water exceeds 3.00 considerably.

*Nitrogen as Nitrites and Nitrates.* — The waters of rivers and wells sometimes contain nitrites and nitrates; they are the products of the decomposition of organic materials and are therefore indicative of sewage contamination. It must be remembered however that the waters from certain geological strata, like the artesian wells in the chalk, contain considerable quantities of nitrates. When these salts are present the water generally has an alkaline reaction, and ammonia is present in but small quantity. Nitrites may be produced in two ways, first, by partial oxidation of organic matter the more complete oxidation producing nitrates, and secondly by reduction of nitrates in presence of excess of organic matter.

The nitrites and nitrates are estimated by reducing them to ammonia and estimating the ammonia by the Nessler test. There are two methods in use for the reduction of the oxides of nitrogen, by means of the copper-zinc couple and by means of aluminium foil.

1. *The Copper-Zinc Method.* — The action of the copper-zinc couple depends on the fact that a thin plate of zinc coated with copper decomposes water and the



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hydrogen evolved is capable of reducing nitric acid in combination, to the state of ammonia.

$$KNO_3 + 4\,H_2 = NH_3 + KHO + 2\,H_2O.$$

The apparatus, *Fig.* 6, *Pl. VI*, is cleaned with distilled water.

Five grammes of the thinnest zinc foil, cut into little squares of the size of a 5 centigramme weight, are placed on a piece of paper. Some *strong* solution of cupric sulphate is introduced into a half-litre flask, in sufficient quantity to cover the zinc foil when introduced, it is gently warmed and the zinc foil passed into the flask, and made to sink by giving the flask a swaying motion.

The copper solution is allowed to act on the zinc for about 10 minutes. When the zinc is well coated with copper, the copper solution is poured off as completely as possible. The flask is filled with water three or four times to wash the couple, and finally 300 c. c. of distilled water are added.

The following is the latest and simplest method for the preparation of the couple. A mixture of two grammes of finely divided copper (obtained by reducing powdered cupric oxide at as low a temperature as possible, and sifting through fine muslin) with 18 grammes of coarse zinc filings, are introduced into a flask of 60 c. c. capacity, provided with a cork, through which passes a tube drawn out to a capillary opening. The flask is heated over a Bunsen flame until the zinc begins to soften, agitating all the time, to insure thorough mixture of the two metals, and to prevent any part from being unduly heated. The mass should consist of grayish-black grains without metallic lustre. As soon as the proper point has been reached the flask is removed from the flame, the agitation being continued for a few seconds to prevent fusion. The point of the capillary tube is then sealed up and the whole is allowed to cool. One-third of this is placed in a flask as before and 300 c. c. of distilled water are added.

Meanwhile 100 c. c. of the water to be examined are evaporated to dryness on a water bath in a porcelain dish 4 inches in diameter. To the solid residue 25 c. c. of distilled water are added, together with a fragment of recently ignited quick lime about the side of a hemp seed, the liquid is boiled, to decompose any urea which may be present, until about 5 c. c. remain. This liquid, together with the washings of the dish containing the residue, is transferred to the flask. A U tube containing 25 c. c. of distilled water is attached to the receiver as represented. The contents of the flask are then distilled over. The first distillate of 50 c. c. is examined by placing 5 c. c. in a cylinder, diluting with distilled water to 50 c. c. and adding 2 c. c. Nessler reagent. The second, third, fourth, and fifth distillates of 50 c. c. each, are Nesslerized without dilution. The contents of the U tube are mixed with 25 c. c. distilled water and Nesslerized.

The ammonia yielded by the chemicals used is determined by making several blank experiments with distilled water, it is about .06 milligramme.

The following calculations are then made : —

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| | | |
|---|---|---|
| (1) | Distillate of 50 c. c. (5 c. c. yielded .07) yielded | .70 |
| (2) | " " " " " | .10 |
| (3) | " " " " " | .05 |
| (4) | " " " " " | .02 |
| (5) | " " " " " | .01 |
| | U tube " | .01 |
| | | .39 |
| | Average of error | .06 |
| | | .83 |

Molecular Weight of $NH_3 = 17$. Atomic Weight of $N = 14$.

$$17 : 14 :: .83 : x = .684 \text{ milligrammes N,}$$

in 100 c. c. of the water. Multiplying by ten gives the milligrammes per litre or parts per million.

2. *The Aluminium Method* — The aluminium method depends on the principle that strong solution of sodium or potassium hydrate dissolves aluminium foil, liberating nascent hydrogen, which acts as in the copper-zinc method.

$$Al + 3\ Na\ HO = 3\ H + Al\ Na_3\ O_3.$$

One hundred c. c. of the water to be examined are introduced into a flask along with 10 c. c. of a ten per cent solution of sodium hydrate and boiled briskly until reduced to one-fourth its bulk. It is then made up to the original bulk with pure water, and when quite cold a piece of aluminium foil about two inches square, rolled around a glass rod to prevent it from floating, is dropped in. To prevent loss of ammonia the opening is guarded by a small tube filled with pieces of pumice of the size of peas (previously ignited for one hour), moistened with pure hydrochloric acid. About six hours afterward the pumice and washings of the tube are added to the liquid in the flask, a Liebig condenser is attached, and the ammonia distilled off and estimated as before.

*Nitrites.* — The most delicate and trustworthy method of estimating nitrites is the following.

The solutions required are, (1) meta-phenylene-diamine, — 5 grammes of the base are dissolved in 1 litre water and slightly supersaturated with sulphuric acid; (2) dilute sulphuric acid, one part of acid to two of water; (3) standard potassium nitrite solution, prepared by dissolving 0.406 gramme pure silver nitrite in boiling distilled water, and adding pure potassium chloride till no more silver chloride is thrown down. This is made up to one litre, the silver chloride allowed to settle and 100 c. c. of the clear solution diluted to one litre. One c. c. is equivalent to 0.01 milligramme $N_2\ O_3$. This solution should be kept in closely-stoppered bottles, quite full.

Four narrow cylinders of colorless glass are required, in which 100 c. c. rise to 17 inches, and which are marked for this capacity.

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One hundred c. c. of the water to be tested are poured into one of the glass cylinders, and one c. c. each of the dilute sulphuric acid and solution of meta-phenylenediamine consecutively added. If a red color is developed on stirring with a glass rod, the experiment must be repeated with less of the water made up to 100 c. c. with distilled water. The dilution is sufficient when the color is just perceptible at the end of one or two minutes. The amount of nitrous acid thus found must of course be multiplied by the coefficient of dilution.

As nearly as possible cotemporaneously with the above experiment, there must be put into three other cylinders 0.3 to 0.2 c. c. of the standard solution of potassium nitrite, filling up each to 100 c. c. with pure water, and adding to each consecutively one c. c. dilute sulphuric acid and one c. c. of the solution of meta-phenylenediamine. The color developed in these cylinders is then compared with that given by the sample of water.

These experiments are repeated by varying the proportions of potassium nitrite solution, until a solution is obtained, of known strength, and exhibiting the same tint as the sample of water. But since the intensity of tint increases with time it is necessary to make a final pair of experiments starting them simultaneously and extending the observation of the shade of color to twenty-five minutes.

In this estimation the water to be examined must be colorless, if tinted the addition of alum or potassium hydrate or carbonate generally precipitates the coloring matter.

Spring waters contain about 3 grammes per litre (or parts per million) of nitrogen as nitrites and nitrates, good river water contains 2 to 4. A water becomes suspicious if it contains from 4 to 10 grammes per litre, and dangerous if it contains 20 grammes per litre. Peaty waters and sewage contain only small quantities; in the latter, putrefaction has destroyed the nitrates. If nitrites abound, the contamination has probably taken place recently. In the late investigations by the National Board of Health it appears that the determination of nitrites and nitrates is of great importance and furnishes most reliable evidence.

**Poisonous Metals.** — The poisonous metals usually considered are lead and copper, the presence of other metals is exceptional.

One hundred c. c. of the water to be examined are placed in a porcelain dish and stirred up with a glass rod moistened with ammonium sulphide. If any coloration is produced a few drops of hydrochloric acid are added, if it disappears at once it was due to iron, if not copper or lead are liable to be present. This qualitative test is sufficient as the mere presence of this metals is sufficient to condemn the water.

**Hardness.** — The hardness of water is either *temporary* or *permanent*. The former is due to the presence of calcium carbonate the latter to calcium sulphate principally. Calcium carbonate is slightly soluble in pure water, 10,000 parts water being capable of dissolving 0.343 parts calcium carbonate at ordinary temperatures;

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but it is much more soluble in water containing carbon dioxide in solution, 10,000 parts water saturated with carbon dioxide at ordinary temperatures dissolving 10 parts. Natural surface waters are never saturated with carbon dioxide but always contain more or less of it, hence, also more or less of calcium carbonate.

Calcium sulphate is more soluble in pure water than calcium carbonate, 10,000 parts water dissolving 20.33 parts at 15° C; the presence of carbon dioxide does not increase the solubility.

The determination of the hardness depends upon the fact that soap will not form a lather with a hard water until all the calcium has been precipitated in the form of insoluble calcium soap,

*Standard Soap Solution.* — Ten grammes pure castile soap are dissolved in a litre of 35 per cent. alcohol. One c. c. of this solution precipitates one milligramme of calcium carbonate. It is liable to lose strength, hence, its strength is verified before use by means of a solution of pure fused calcium chloride 1.11 grammes to the litre of water. One c. c. soap solution should precipitate all the calcium in one c. c. calcium chloride solution.

To perform the test 70 c. c. of the water to be examined are placed in a stoppered bottle, capacity about 250 c. c., and standard soap solution added by means of a pipette graduated to $\frac{1}{10}$ c. c. After each addition of the soap solution the bottle is shaken, and when a lather begins to form it is laid on its side. The lather should remain permanent for five minutes. The stopper is removed after each shaking to allow the escape of gas. The number of c. c. of soap solution required gives the degree of hardness, which is recorded as so many *degrees*.

Temporary hardness may be remedied in small quantities of water by boiling, which expels the free carbon dioxide, thus precipitating the calcium carbonate. In large quantities of water the usual method is by addition of lime, which combines with the free carbon dioxide and is precipitated as calcium carbonate, also precipitating the calcium carbonate previously in solution. Moderately hard waters are more palatable than soft waters, good waters average between 3 and 14 degrees.

**Sulphates.** — The sulphates most commonly present in water are those of calcium, magnesium, and sodium; they are objectionable when in excess, principally on account of their purgative properties.

About 10 c. c. of strong barium chloride solution are placed in a beaker, acidified with a few drops of pure hydrochloric acid and 100 c. c. of the water to be examined are added, the contents of the beaker boiled and then the precipitate is allowed to settle. After 2 hours it is filtered through the best Swedish filter paper, the beaker washed out with hot distilled water, the washings being passed through the filter; the filter is then dried over a lamp, ignited in a platinum crucible and weighed. The weight of the crucible and of the filter ash is subtracted. The number of milligrammes obtained multiplied by ten gives the milligrammes per litre. This

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is multiplied by $\frac{80}{233}$ (the amount of $SO_3$ in one part $BaSO_4$, the precipitate), and recorded as parts of sulphuric oxide ($SO_3$) per million.

**Microscopic Examination.** — The microscopic examination of a drinking water is generally made by allowing the suspended matters in a sample of water to subside in the sample bottle. The greater part of the water is then decanted, and that at the bottom of the bottle, containing the sediment, is poured into a conical glass. After subsidence a drop is removed by means of a pipette, placed on the slide of a microscope, covered with thin glass and examined at once, or is allowed to evaporate and then examined.

Mineral gritty matters, clay silt and sandy particles are noticed. Soluble salts are recognized by their crystalline form and by the action of the ordinary reagents. The kind of suspended matter furnishes a clue to the character of the impurities, thus fibres of clothing indicate slops, epithelium and the eggs and joints of the tape-worm indicate animal sewage, algæ and fungi indicate vegetable impurities.

It is possible that the germs of zymotic diseases may be carried by these organisms, but the microscopic investigations of the sediment of drinking water have not yet discovered the *germs* of disease. That many diseases are due to germs has been proven without a doubt. Pasteur has discovered the germs of several diseases, that of splenic fever, for instance, he found to be a large bacterium. But many of the bacteria are exceedingly minute, and may be transparent and thus rendered invisible. Many germs undergo changes and become invisible, thus the germ of fowl-cholera is distinctly visible under the microscope, but preserved in a closed tube it soon disappears and is no longer visible under the microscope; if now a needle be dipped into the liquid and then inserted in the cutaceous tissue of a fowl in a few days the fowl will be dead, proving that the germ is still there. Thus the problem is a very difficult one.

Biological investigations made by injecting waters known to be dangerous into rabbits and other animals have been thus far more or less unsatisfactory.

**Interpretation of Results.** — Some thirty years ago it was discovered that cholera was transmitted by drinking water. This transmission of cholera as well as that of typhoid fever has been proven without a doubt. No doubt they are transmitted in other ways, but this is undoubtedly one of the methods. There is considerable evidence that diptheria may be thus transmitted. Dysentery has been produced by bad water.

Waters known to have produced disease are generally found to contain organic matter, suspended or dissolved. This impurity may not be noticed, for a water may be clear and colorless and have a good refreshing taste, and yet be very dangerous. Water free from contamination with human sewage has never been proved to infect with cholera or typhoid fever, but diseases of other kinds have been caused by mineral matters or by vegetable matters, dissolved or suspended.

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Peaty waters are an exception, they contain much vegetable organic matter, but not in a state of easy decomposition like that from marshes, hence, they sometimes furnish excellent waters, that of the Dismal Swamp is preferred for carrying to sea on account of its keeping qualities.

Suspended mineral matters are liable to produce dysentery, in certain districts in India this disease has been traced to minute scales of mica in the water. Dissolved mineral matters may also be injurious, some causing dyspepsia, others, on account of their purgative properties, producing diarrhœa.

The great sources of danger in cities are sewage and refuse from factories, especially when river water is the source of supply.

When wells are used as a source of drinking water great care must be taken that there is no privy or cesspool within a radius of twice the depth of the well, especially in sandy soil.

In all analyses of drinking waters duplicate and even triplicate estimations should be made. The results are properly recorded in tables and compared.

According to the standards of purity generally adopted a good drinking water should not contain more than

| | | | | |
|---|---|---|---|---|
| Total solids, | 400. | parts | per | million. |
| Chlorine, | 70. | " | " | " |
| Oxygen consumed in 3 hours, | 1. | " | " | " |
| Free Ammonia, | .02 | " | " | " |
| Albuminoid Ammonia, | .08 | " | " | " |
| Nitrogen as Nitrites and Nitrates, | 5. | " | " | " |
| Nitrogen as Nitrites, | 0. | " | " | " |
| Poisonous metals, | 0. | " | " | " |
| Hardness, | 14°. | | | |
| Sulphuric oxide ($SO_3$), | 70. | " | " | " |

According to the investigations of the National Board of Health, standards of purity for any *one* of the above estimations are worthless, except as *local* standards. Nevertheless they are useful in comparing the evidence furnished by all the estimations. Very good and very bad waters are generally easily determined, but most waters are intermediate and must be classed as of doubtful purity, hence, the great difficulty of deciding upon a given sample.

The following examples may serve as guides.

Diagnosis of water polluted by vegetable matter.

| | |
|---|---|
| Free Ammonia, | No excess. |
| Albuminoid Ammonia, | Large excess. |
| Chlorine, | Insignificant. |
| Nitrogen as Nitrites and Nitrates, | " |

Peaty waters are generally very soft and the amounts of free and albuminoid ammonia are about equal.

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Diagnosis of pollution by animal matter.

| | |
|---|---|
| Free Ammonia, | Excess. |
| Albuminoid Ammonia, | " |
| Nitrogen as Nitrites and Nitrates, | " |

Diagnosis of pollution by contents of sewers.

| | |
|---|---|
| Free Ammonia, | Large excess. |
| Albuminoid Ammonia, | Excess. |
| Chlorine, | Excess. |
| Nitrogen as Nitrites and Nitrates, | If sewage passes directly into water — none, if it travels through intermediate earth — excess. |

Much nitrogen as nitrates and nitrites and excess of oxygen consumed show recent contamination. Much nitrogen as nitrites and nitrates and little oxygen consumed show that more or less complete conversion of the organic matter has taken place.

Diagnosis of pollution by excremential filth.

| | |
|---|---|
| Free Ammonia, | Enormous excess (.50 to 2.0). |
| Albuminoid Ammonia, | Excess (.3 to .6). |
| Chlorine, | Generally in large excess. |
| Nitrogen as Nitrites and Nitrates, | In either minute amount or in large excess. |

To distinguish such a water from rain-water, the rate of distillation of the ammonia is noticed, in rain-water it comes off much more gradually. The latter also contains little chlorine (except near the sea), is soft and contains but a small amount of nitrogen as nitrites and nitrates.

Diagnosis of pollution by gaseous emenations.

| | |
|---|---|
| Free Ammonia, | Excess. |
| Albuminoid Ammonia, | Excess. |
| Chlorine, | Little. |
| Nitrogen as Nitrites and Nitrates, | Excess. |

No disease has ever been proved attributable to living organisms in drinking water. Certain forms of life are peculiar to certain waters, and river, pond and spring waters have peculiar but also common forms. Certain others seem to be peculiar to sewage, but no definite results have been reached in the investigations. *Fig.* 7, *Pl. VI*, illustrates the organisms found in the water supplied to London during the cholera epidemic of 1851 and 1854. Many of them are present in the Schuylkill river now.

**Purification of Water.** — Water is purified in nature by the action of the air, which oxidizes the organic matter, by subsidence, by filtration through porous strata and by evaporation and condensation. It is purified artificially by aeration, by boiling, by filtration, by distillation, or by chemical means.

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Aeration increases the rate of oxidation of the organic matter, but it has been found in practice that the action is too slow to furnish an available method for the purification of water on a large scale.

Boiling removes lime and magnesia, and destroys some of the organic matter. Whether germs of diseases like cholera are destroyed is still a question. Nevertheless, this method is one of the most practically useful means of rendering water more palatable. It also removes coloring matter and odors.

Filtration is the method in common use. It removes, principally, suspended matters, but also, to a great extent, dissolved organic matter. The latter action is supposed to be due to the property of the filtering materials of condensing oxygen in their pores, thus destroying the dissolved organic matter by oxidation. Many substances have been recommended and used at different times, wool, sponges, sand, powdered coke, pumice, charcoal, etc., but, on the small scale, animal charcoal and spongy iron have been found to possess the greatest purifying powers, and are now very generally used for domestic filters. The filtering power of spongy iron has been lately tested at Antwerp on a large scale, and the results indicate not only its value in this respect but also that there is no necessity for renewing the iron.

*Fig.* 8, *Pl. VI*, represents an ordinary filter for domestic use. The water is poured into the tub *l*, passes through the perforated bottom into *b*, where sediment is deposited, then through the tube *d* into *c*, whence it rises through the layers of sand and animal charcoal into the reservoir of filtered water *k*. To clean the filter it is only necessary to reverse the current by opening the stop-cock *m*.

The filtration of the waters of large reservoirs is generally accomplished by means of layers of sand and gravel. *Fig.* 9, *Pl. VI*, represents one of the filters of the London water-works. The water enters the filter by the central canal, passes through the filtering layers, is collected by the small canals *c* of perforated bricks, and discharged through the lower canal *a*. The filtering layers consist of *d* coarse stones, *e* smaller stones, *f* coarse gravel, *g* fine sand. *b* is an air-tube rising from the lower canal.

Distillation removes every *solid* impurity but does not free water from ammonia, carbon dioxide and other volatile substances. To avoid impurities, the first fifth of the distillate and the last fifth of the water to be distilled are rejected. The addition of lime or potash and of potassium permanganate previous to distillation facilitates the removal of the ammonia. Distillation is especially useful to prepare water at sea and also for chemical purposes. It is apt to be insipid in taste unless air is forced into it, the dissolved air having been removed in the process.

The principal chemical methods in use for the purification of water are Clark's Process, the Permanganate Process, and the Alum Process. Clark's process consists in adding lime-water to temporarily hard waters, in the proper quantity. Not only is the water rendered soft, but a large proportion of the organic matter, and any coloring matter that may be present, are thereby removed. Care must be taken



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not to add excess of lime, which would render the water alkaline. This is easily determined by testing a portion with silver nitrate solution, excess of lime gives a brown precipitate, hard waters a white one. This process is used in the English water-works. The Permanganate Process consists in adding a little lime water and then sufficient potassium permanganate to produce a faint pink tint at the end of fifteen minutes. The excess of lime is sometimes precipitated with acid sodium carbonate, the liquid neutralized with a little hydrochloric acid, thus liberating carbon dioxide and rendering the water more palatable. Alum has been used in France and China. It has a mechanical action, due to the separated alumina, of throwing down suspended impurities. About 6 grains to the gallon are used.

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| DATE. | | ances. | Poisonous Metals. | | CHARACTER. | REMARKS. |
|---|---|---|---|---|---|---|
| Aug. 13th, 1869. | Ra | ..... | ..... | ..... | Very Good. | Clear. |
| | Pu c | ..... | ..... | ..... | Very Good. | ..... |
| | W | ..... | ..... | ..... | Good. | ..... |
| | Lo | ..... | ..... | ..... | Very Good. | ..... |
| | Sh | ..... | ..... | ..... | Good. | ..... |
| | W | ..... | ..... | ..... | Polluted. | ..... |
| | Pu | ..... | ..... | ..... | ..... | Mineral Water. |
| June 5th, 1872. | W | ..... | ..... | ..... | Highly Polluted. | ..... |
| | Ar | ..... | ..... | ..... | ..... | ..... |
| | Lo | ..... | ..... | ..... | Good. | ..... |
| Feb. , 1878. | Su S | ..... | ..... | ..... | ..... | Slightly Turbid. |
| | Lo | ..... | ..... | ..... | Excellent. | ..... |
| | Rh | ..... | ..... | ..... | ..... | ..... |
| | Rh | ..... | ..... | ..... | ..... | ..... |
| | A | ..... | ..... | ..... | ..... | ..... |
| | Fr | ..... | ..... | ..... | Bad. | ..... |
| May 29th, 1880. | W | ..... | ..... | ..... | ..... | After long drought |
| 1875. | Sc | ..... | ..... | ..... | Very Good. | Phila. supply. |
| Aug. 12th, —— | W | ..... | ..... | ..... | } Infecting with Typhoid Fever. | } During prevalence of Epidemic. |
| Aug. 21st, —— | W | ..... | ..... | ..... | | |

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# SECTION 6.

## Air.

The air is the gaseous matter surrounding the Earth. The phenomena mainly depending upon it are the weather, solar and terrestrial radiation, the disintegration of rocks, animal and vegetable life, and the propagation of sound.

Air is a mechanical mixture of gases. Pure air contains:

| | | |
|---|---|---|
| Oxygen, | 209.6 | in 1000 volumes. |
| Nitrogen, | 790.0 | |
| Carbon dioxide, | .4 | |
| Moisture, | varying with temperature. | |
| Hydrogen dioxide, Nitrous acid, Nitric acid. | | occasional components. |
| Organic matter, Ammonia, | | very minute traces. |

Air is here considered merely in its relations to animal life. The oxygen is the constituent essential to animal life, the nitrogen acting merely to dilute the oxygen. In respiration the mixture of these gases is taken into the lungs, is absorbed through the membranes of the capillaries and thence passes into the blood. It is used up in oxidising the carbon and hydrogen of the animal tissues, in the capillaries throughout the body. It is returned to the lungs and is given off in expiration as carbon dioxide and water.

A complete volumetric analysis of air requires expensive and complex apparatus, and great skill and considerable time in its manipulation. The main practical question to be answered is whether any given air is, or not, deliterious to health, and this can generally be determined by simple processes.

The air is rendered impure by the presence of floating matters, organic and inorganic, and by the volatile products of chemical changes taking place in nature, principally the decay of organic matter.

**Solid Bodies in the Air.** — The solid bodies in the air consist of various mineral, vegetable and animal matters, — sodium chloride, soot, straw, rags, pollen, seeds and spores, cells, epithelium, fungi, etc.

The method used at the Montsouris Observatory for collecting the dust of the air, is represented in *Fig.* 1, *Pl. VII.* The receiver is a bell glass, the roughened lower edge resting on a piece of roughened plate-glass. The upper opening is closed by a cork perforated by two holes, through which pass glass tubes, one, *c*, connecting an aspirator, the other, *h*, terminating in a tapered point a short distance above a glass slide covered with glycerine or syrup. Air is drawn through the apparatus by means of the aspirator, and after a sufficient amount of dust has collected on the slide it is examined under the microscope.

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The solid matter found in the air of the accident ward, St. Mary's Hospital, London. is represented in *Fig.* 5, *Pl. VII*.

1. Epidermis of hay with fungus attached.
2. Linen Fibre.
2′. Fungus filament.
3. Nucleated epithelium from the mouth.
3a. Pus cells.
4. Worn epithelium from the skin.
4a. Charred vegetable particles.
4d. Fungus spores.
5. Cotton fibre.
6. Woolen fibre.
7. Fragments of insects.
8. Pine pollen.
9. Dried-up palmellaceous frond.
10. Ciliated spore, probably from vaucehria.

The weight of the solid matter in a given volume of air is determined by passing it through a U-shaped, platinum tube, 7 inches long, ¼ inch in diameter, containing asbestus at the bend. Little caps of fine platinum gauge are inserted at each end of the asbestus to prevent loss. The tube is weighed before and after the passage of the air, the difference determines the weight of solid matter. By igniting the tube it may be again used without renewing the asbestus.

**Organic Matter.** — The organic matter in the air is derived from various sources, especially from the skins and lungs of all animals; in a close room its odor is readily detected. It is difficult to determine its amount, as it is present in such small quantities.

The simplest method for its determination is to pass a certain quantity of air by means of an aspirator through a series of four wash bottles, of 100 c. c. capacity, each containing 50 c. c. of *pure* distilled water. Into the first bottle 50 c. c. of pure hydrogen chloride are also poured. These air-washings are distilled with caustic potash and potassium permanganate, and the distillate is Nesslerized, as in the analysis of potable water.

The best method for collecting the air-washings is represented in *Fig.* 2, *Pl. VII*.

A is a glass cylinder 8 inches long, 2 inches in diameter, furnished with a perforated rubber stopper E, through which passes the air-pipe of a Bergson's spray-producer C, and also a straight glass tube ¼ inch in diameter, 12 inches long. B B are Woulfe's bottles, capacity 130 c c., with rubber stoppers. D is a black ½ oz. india-rubber ball, to which a glass tube, drawn out to a fine point, is fitted.

To carry on an examination the several parts of the apparatus are cleansed with double-distilled water, by the aid of the ball injection tube D. From a flask containing 100 c. c. distilled water a little is poured into the cylinder, so that when

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inverted its level shall be at F, below the jets. The remainder is poured into the wash bottles. Air is pumped into the cylinder by means of the spray-producer (whose capacity is previously determined). The rubber balls are squeezed empty of air about 540 times, or until at least one cubic foot (about 28,317.6 c. c.) has passed into the glass cylinder. The water in the cylinder and wash-bottles is returned to the flask, the cylinder, wash-bottles, and glass tubes are washed out with not more than 30 c. c. of double-distilled water, by means of the tube D, and the washings added to the water in the flask.

The mere washing of the apparatus, before and after the operation, increases the error, hence this is determined previously, by washing the clear apparatus with double-distilled water, determining the organic matter as presently to be described, and multiplying by two. It is about .006 mg. of albuminoid ammonia for one cubic foot of air. This amount should be deducted from the result of each analysis.

The organic matter is determined, as in the analysis of potable water by the albuminoid-ammonia process. The stoppered retort, capacity 200 c. c., rests in a copper basin containing sand, and is connected with a small glass Liebig's condenser. The apparatus is carefully washed, then double distilled water is distilled through it. No corks are used in the connections, only rubber stoppers. The air-washings are introduced into the retort and distilled. The distillate is received into small Nessler glasses, 4 inches long, $\frac{5}{8}$ inch in diameter, marked at 10 c. c. The first distillate of 10 c. c. is Nesslerized by adding $\frac{1}{2}$ c. c. Nessler reagent. The very dilute standard ammonia solution used is prepared by mixing 5 c. c. of the strong solution (one milligramme in one c. c.) with 995 c. c. of double-distilled water. One-tenth c. c. contains .0005 milligramme $NH_3$. The burette should be one foot long and $\frac{3}{10}$ of an inch in diameter.

The second, third, and fourth distillates of 10 c. c. are thrown away, $\frac{1}{3}$ being added to the ammonia found in the first for the total free ammonia. The contents of the retort are allowed to cool until tepid, 10 c. c. of the solution of potassium hydrate and potassium permanganate are added, and the distillation continued. Three distillates of 10 c. c. are obtained and Nesslerized with $\frac{1}{2}$ c. c. of Nessler reagent.

Pure air contains about 0.08 milligrammes of albuminoid ammonia in the cubic metre.

| | Milligrammes per Cubic Metre. | |
|---|---|---|
| | Ammonia. | Albuminoid Ammonia. |
| Pure air of Meadow, Essex. | .066 | .044 |
| Hyde Park, London. | .028 | .086 |
| Rooms, Officers' Quarters, Portsmouth. | .436 | .462 |
| No. 5 Ward of Hospital, Portsmouth. | .428 | 1.307 |



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**Carbon Dioxide.** — Carbon dioxide is supplied to the air mainly by oxidation of carbon, as in ordinary combustion and in the respiration of animals. An average man gives off 0.6 cubic foot of carbon dioxide every hour. The city of Manchester, by combustion of coal, etc., gives out daily 15,000 tons of carbon dioxide. It is prevented from accumulating to a great degree in particular localities by the diffusive power of gases, and is removed from the atmosphere by vegetation.

Carbon dioxide is essential to vegetable life, and is not injurious to animal life when present in the proportions found in pure air. When present in larger proportions it acts as a poison to animal life, by preventing the diffusive action, in the capillaries of the lungs, of the passage inward of the oxygen of the air, and outward of the carbon dioxide in the blood.

1 *Method.* — The carbon dioxide in a given volume of air may be estimated by passing one cubic foot of air per hour, for 48 hours, through a solution of potassium hydrate contained in three wash-bottles. The contents are collected, barium chloride is added, and the resulting precipitate is washed, dried, ignited and weighed.

$$CO_2 + 2\ KHO = K_2\ CO_3 + H_2\ O.$$
$$K_2\ CO_3 + Ba\ Cl_2 = Ba\ CO_3 + 2\ K\ Cl.$$
$$Ba\ CO_3\ (\text{heated}) = Ba\ O + CO_2.$$

The amount of $CO_2$ is computed from the weight of Ba O obtained.

2 *Method.* — Pettenkofer's method gives good results, but requires time and labor. A glass vessel, capacity about 4.5 litres, is taken, its capacity accurately determined in c. c., dried and filled with the air to be examined by means of a bellows. Sixty c. c. of lime or baryta water are put in, and the mouth is closed with a rubber cap. The vessel is agitated and then allowed to stand, for one hour if baryta water has been used, for 8 hours if lime water has been used. The carbon dioxide combines with part of the baryta or lime, thus diminishing the causticity of the solution. The amount of this diminution is a measure of the carbon dioxide absorbed. Neutralization of the baryta or lime is effected by means of oxalic acid :

$$C_2\ H_2\ O_4\ .\ 2\ H_2\ O + Ca\ O = Ca\ C_2\ O_4 + 3\ H_2\ O.$$
$$126 : 56 :: 1 : x = 2.25.$$

Hence, 2 25 parts oxalic acid are required to neutralize one part lime. 2.25 grammes oxalic acid are dissolved in one litre water. one c. c. will neutralize one milligramme of lime. Thirty c. c. of the original lime water are exactly neutralized with the oxalic acid solution, using litmus paper as an indicator; this determines the strength of the lime water. Thirty c. c. of the lime water, which has absorbed the carbon dioxide in the given volume of air are also neutralized with the oxalic acid solution. The difference determines the lime precipitated by the carbon dioxide absorbed, from which the amount of carbon dioxide can be computed.

$$Ca\ O + CO_2 = Ca\ CO_3$$

The weight of the lime precipitated is to the weight of the carbon dioxide as 56 : 44, hence, the weight of the carbon dioxide is $\frac{44}{56}$ of the weight of the lime.

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Now, one c. c. $CO_2$ at 0° C weighs 1.9767 milligrammes, hence, one milligramme is $\frac{1}{1.9767}$ c. c. in volume. The volume of carbon dioxide is therefore $\frac{44}{56}$ of $\frac{1}{1.9767}$ of the weight of the lime precipitated, and as only half the lime water used was tested, this is to be multiplied by 2, giving as a multiplier $2 \times \frac{44}{56} \times \frac{1}{1.9767} = 0.795$. The difference, obtained in the neutralization above, multiplied by 0.795 gives the total carbon dioxide in volume. If now 60 c. c. (occupied by the lime water) be deducted from the capacity of the jar, and the volume of carbon dioxide be divided by the corrected capacity, the quotient will be the volume of carbon dioxide, measured at 0° C, per volume of air. If the air is not at 0° C a correction for temperature must be made. If the temperature was 15° C, then, the volume of air being $a$, its volume at 0° C would be obtained by the proportion,

$$273 : 273 + 15 :: a : x = \text{Answer.}$$

3 *Method.* — The minimetric method consists in ascertaining the smallest amount of air required to produce a precipitate of given density. A weak solution of barium hydrate is employed (.1 to .5 per cent.). Barium hydrate, it is well to remember, is very poisonous. A standard precipitate is obtained by shaking ½ oz. baryta water in a 2½ oz. bottle in pure air, which generally contains .04 per cent. of carbon dioxide. The liquid becomes translucent. A word is written in lead-pencil on paper in such a depth of shade that the tubidity of the liquid just prevents it from being seen, when viewed through the liquid in the bottle. One-half ounce baryta water is placed in a bottle which holds exactly 2½ oz., the air having previously been changed by a few strokes of the finger pump, *Fig.* 3, *Pl. VII*. The 2 ounces of air are shaken with the ½ ounce of baryta water; two ounces of air are again pumped in and again shaken, and so on until the word in lead-pencil just becomes invisible. Then, by means of the following table the carbon dioxide is determined. Instead of the valves a simple slit in the rubber tube of the ball pump is sufficient, and serves the same purpose, (*Fig.* 4, *Pl. VII*).

| Number of Ballfulls of Air. | Volumes of Carbon Dioxide in 100 of Air. | | Number of Ballfulls of Air. | Volumes of Carbon Dioxide in 100 of Air. | |
|---|---|---|---|---|---|
| | 2 oz. Ball. | ½ oz. Ball. | | 2 oz. Ball. | ½ oz. Ball. |
| 1 | .44 | | 13 | .034 | .13 |
| 2 | .22 | | 14 | .032 | .12 |
| 3 | .14 | | 15 | .029 | .116 |
| 4 | .11 | | 16 | | .11 |
| 5 | .088 | | 17 | | .10 |
| 6 | .074 | | 18 | | .098 |
| 7 | .063 | | 19 | | .093 |
| 8 | .055 | | 20 | | .088 |
| 9 | .049 | | 21 | | .084 |
| 10 | .044 | .17 | 22 | | .08 |
| 11 | .040 | .16 | 23 | | .077 |
| 12 | .037 | .14 | 24 | | .074 |

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The baryta water is stored as represented *Fig.* 6, *Pl. VII*. The U tube contains fragments of pumice moistened with caustic potash.

Carbon Dioxide in 1000 Volumes of Air.

| | $CO_2$ in external air. | $CO_2$ in room. |
|---|---|---|
| Aldershot Barracks. | 0.440 | 1.408 |
| Tombs Prison, New York. | | 1.47 |
| Portsmouth Garrison Hospital. | 0.306 | 2.057 |
| Aldershot Military Prison. | 0.409 | 3.484 |
| Ward-room of "Alert," Arctic Expedition, 1875–6. | | 4.82 |
| Girls school room of 10,400 cubic feet, for 70 girls. | | 7.23 |

**Noxious Gases.** — The noxious gases in the air result principally from the putrefactive decay of animal and vegetable matter. They are sulphydric acid gas, ammonia and ammonium sulphide. Sulphydric acid gas, $H_2S$, is readily detected by means of lead papers (papers moistened with lead acetate), which are blackened by a trace of the gas. Ammonia is detected by moist red litmus paper, which is turned blue thereby, or, when present in large quantity, as in the air of stables, by the fumes produced on a glass rod which has been dipped in hydrochloric acid. Ammonium sulphide is detected by paper dipped in sodium nitro-ferricyanide, which produces a transient but splendid purple color.

**Purification of Air.** — The natural methods of purification of the air are by diffusion, dilution, transference by winds, oxidation and reduction, and the fall of rain. The most effective artificial method is ventilation. For proper ventilation 1000 cubic feet of air, per man, per hour are required. Chemical agencies have some effect in aid of ventilation. The impurities which can be removed by chemical means are carbon dioxide, sulphydric acid gas, ammonium sulphide, ammonia and organic matter. The chemical agents used are called *disinfectants*.

Charcoal has the power of absorbing noxious gases, and by condensation in its pores causes the oxidation and destruction of organic matter. It is exposed to the air in bags or shallow pans. Animal charcoal and the residue of the distillation of bituminous coal are the best forms for this purpose.

Lime absorbs carbon dioxide and sulphur compounds.

Potassium permanganate, zinc chloride and lead nitrate absorb sulphydric acid gas. The permanganate also oxidises organic matter and thus destroys it. The solutions of these salts are exposed in flat dishes or else cloths are dipped in them and exposed to the air.

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Chlorine is one of the best disinfectants known, it decomposes sulphydric acid gas on account of its affinity for hydrogen, and destroys germs, and organic matter generally, by virtue of the same property. It is generally prepared for this purpose by exposing moist "chloride of lime" to the air, the salt is decomposed by the carbon dioxide of the air and the chlorine thus liberated.

Nitrous acid, prepared by placing copper in nitric acid and water, has great oxidising properties and is the best substance known to remove the smell of the dead-house.

Sulphurous oxide, prepared by burning sulphur, decomposes sulphydric acid gas and destroys organic matter.

Carbolic acid diminishes the rapidity of the putrefaction of animal matter and arrests the growth of fungi.

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## SECTION 7.

### The Army Ration.

The importance of a proper issue of food to the soldier, not only at critical movements, but also under ordinary circumstances in camp or barracks, cannot be overrated. Good food contributes largely to the health of the soldier, and when it is remembered that many more die from disease than from wounds in the course of a war its great importance is at once apparent.

The statistics of our late war give:

| | | |
|---|---|---|
| Killed, | 44,238 | 93,443. |
| Died of wounds, | 49,205 | |
| Died from disease, | | 186,216. |
| Discharged on account of wounds, | | 48,374. |
| Discharged on account of disease, | | 136,584. |

In our army the Captains are directly responsible for the condition of the food issued to their companies. To meet this responsibility a proper knowledge of food, of the general principles of dietetics of the various effects of cooking, and of the special methods for detecting ordinary adulterations, is essential.

### *Food.*

Food is derived primarily from the vegetable kingdom. The vegetable products are built up through the agency of the heat and light of the sun. The force so employed becomes stored up in the plant, and is ready to be liberated under favorable conditions. It is generally liberated in the animal by oxidation, and its amount must be, according to the principle of the Conservation of Energy, exactly the same as that originally made use of, provided the oxidation be complete. This is not generally the case, however, as many substances are eliminated, in the processes of animal life, in an imperfectly oxidised state, so that they are still capable of producing force.

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The direct objects of food are the renovation of the tissues and the production of heat or other forms of force. The principal ultimate objects of food are : —

Maintenance of Animal Temperature,
Internal physical work,
Brain work, and
External work.

The total force obtainable from the typical daily diet of Moleschott ($p$ —) is, by calculation and experiment, about 8,000,000 foot pounds, of which less than one-fifth is available for external work. The internal physical work consists mainly of circulation and respiration, the former is about 600,000, the latter about 125,000 foot pounds.

Muscular work is not be referred to an oxidation of the nitrogenous basis of muscular and nervous tissue, but to that of hydro-carbonaceous matter. The former is the instrument of action, the latter the motive power.

The principal elements present in food are carbon, hydrogen, oxygen, nitrogen.

Carbon is derived from the carbon dioxide of the atmosphere. The green parts of plants, under the action of the sun's heat and light, decompose the carbon dioxide, assimilating the carbon and eliminating the oxygen.

Hydrogen and oxygen are derived principally from water, which is either assimilated as such, or is decomposed, and its elements assimilated in various proportions.

Nitrogen is not assimilated directly from the free nitrogen of the air, but is derived from ammonia, a constant constituent of the atmosphere. The ammonia enters the plant by the roots in the form of carbonate, sulphate or humate.

The other elements found as constituents of the human body are sulphur, phosphorus, chlorine, sodium, potassium, calcium, magnesium, iron, fluorine, silicon, manganese, aluminium and copper. The elements are not available, directly, as food, but must be in combination, and, generally, in the form of *organic* compounds.

Food is subdivided as follows : —

1. Organic. { Nitrogenous. / Non-Nitrogenous. { Fats. / Carbo-hydrates.
2. Inorganic.

**Nitrogenous Food.** — The nitrogenous alimentary principles contain the elements carbon, hydrogen, oxygen and nitrogen, and sometimes also sulphur and phosphorus. The principal forms are albumen, fibrine and caseine. These principles exist both in the animal and in the vegetable kingdom.

This class of food is merely comminuted in the mouth. It is digested, or rendered highly soluble, and converted into a highly diffusive liquid, in the stomach, by the action of the gastric juice. The latter is acid in its reaction and contains a nitrogenous principle, *pepsin*. The action of the gastric juice is assisted by the elevated temperature of the body and the movement of the walls of the stomach. The food then passes into the small intestine, where it is acted upon by the intestinal secretion,

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secreted by the walls of the intestine. Into this intestine also pass the secretions of the pancreas and of the liver. The nitrogenous matter becomes metamorphosed and is rendered capable of being absorbed by the lacteals and thus passes into the blood.

The principal object of nitrogenous food is to supply material for the development and renovation of the tissues. As nitrogen is an essential constituent of the various textures of the body, nitrogenized compounds are necessary to their growth and repair.

**Non-Nitrogenous Food.** — The non-nitrogenous alimentary principles contain the elements carbon, hydrogen and oxygen, and may be divided into the two classes: 1. Fats, and 2. Carbo-Hydrates.

*Fats.* — The fats contain only a small proportion of oxygen, their average composition being represented by $C_{10}\ H_{16}\ O$.

Fat is not altered by the saliva or the gastric juice, but is digested by the pancreatic fluid in the small intestine. This action consists in emulsification or reduction to a state of minute subdivision, the fat being thus rendered capable of absorption by the villi, little projecting bodies in the small intestine, communicating with the lacteals, by means of which the fat passes into the blood.

The purposes to which fat is applied in the system are the formation and deposition of adipose tissue, and the production of heat by oxidation.

Adipose tissue is deposited in the body directly from the blood, and fulfills various purposes. It fills up interstices between muscles, bones and vessels, gives a round form to the body, and acts as a bad conductor of heat, thus retaining the animal warmth. It is susceptible of reabsorption into the blood, and thus constitutes a store of force production to be drawn upon as circumstances may require.

Fat is essentially a calorifacient agent. Its heating power by combustion is evident from the typical symbol $C_{10}\ H_{16}\ O = C_{10}\ H_{16}\ (H_2\ O)$, since, not only is the carbon, but also nearly all the hydrogen, in an unoxidised state. The heat produced by the oxidation of non-nitrogenous matter appears as heat, or is converted into muscular and nervous force. The oxidation takes place, in all probability, not in the blood, as it circulates through the capillary vessels of the muscle, but in the muscle tissue itself. One gramme beef-fat burned in oxygen produces 9,069 heat units, from which 3,836 kilogrammetres (27,783 foot-pounds) of mechanical work are obtainable.

Nitrogenous matter may also serve to produce heat, but in this case it is split up by the liver into two portions, one nitrogenous and the other non-nitrogenous, the former contributing to the production of muscle, the latter to that of heat.

**Carbo-Hydrates.** — These contain the same elements as the fats, viz: — carbon, hydrogen and oxygen, but the latter are exactly in the proportion to form water. Starch, $n\ C_6\ H_{10}\ O_5 = n\ [C_6\ (H_2\ O)_5]$, and cane sugar, $C_{12}\ H_{22}\ O_{11} = C_{12}\ (H_2\ O)_{11}$, may be taken as types.

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Starch is acted upon by the saliva of the mouth, and partially converted, by its active nitrogenous principle, *ptyalin*, into dextrine and then into grape sugar, but the main part of the digestion is accomplished by the intestinal secretion. Cane sugar is probably first converted into grape sugar, and is then acted upon by the liver and converted into *amyloid substance*, (Glycogen, n $C_6 H_{10} O_5$). Amyloid substance, derived from sugar or starch, is finally deposited as fat.

**Inorganic Food.** — Organic matter alone will not suffice for the maintenance of vital action. Certain inorganic compounds are necessary in the processes of animal life, thus water acts mainly as a solvent, and furnishes a medium of circulation. Other compounds are found to be essential constituents of the various component parts of the animal fabric and of the secretions, hence, they must be supplied in the food. The chief saline principles present are compounds of calcium, magnesium, potassium, sodium and iron, with chlorine, phosphoric, carbonic and sulphuric acids.

*Principles of Dietetics.*

To determine the necessary kind of food, the natural diet, milk, is usually used for comparison. It contains all the alimentary principles necessary to support life in the young of animals.

| | |
|---|---|
| Water, | 88 per cent. |
| Fat (cream or butter), | 3 " " |
| Nitrogenous matter (albumen and caseine) | 4 " " |
| Carbo-Hydrates (lactine) | 4½ " " |
| Inorganic matter (calcium phosphate, sodium chloride, iron, etc., | ½ " " |

It was inferred from its composition, and has been proven by numerous experiments that a *mixed diet* is necessary for the continued and proper support of life.

The daily amount of food required by an ordinary working man, of average height and weight, as determined by experiment, is (Moleschott) : —

| Dry Food. | oz. avoir. |
|---|---|
| Nitrogenous matter, | 4.587 |
| Fatty matter, | 2.964 |
| Carbo-Hydrates, | 14.250 |
| Salts, | 1.058 |
| Total | 22.859 |

By calculation from this table it is found that the daily requirements are,

| | |
|---|---|
| Carbon, | 4800 grains |
| Nitrogen, | 300 " |

It is also found that the amounts excreted daily by the lungs, skin, kidneys and bowels are,

| | |
|---|---|
| Carbon, | 4694 grains |
| Nitrogen, | 307 " |

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The proper proportion of carbon to nitrogen in food is, therefore, about as 16 : 1. Now, in bread the proportion of carbon to nitrogen is 30 : 1, hence, the bread which would furnish the necessary nitrogen, 300 grains, would also furnish 9000 grains of carbon, or twice as much as is necessary; in meat the proportion of carbon to nitrogen is 16 : 4½, hence, the meat required to furnish 300 grains of nitrogen would only furnish 1117 grains carbon, or less than one-fourth the required quantity. A mixture of 2 lbs. bread and ¾ lb. meat will furnish a sufficient quantity of both elements, hence the *economy* of a mixed diet.

According to Moleschott's table, 23 oz. of anhydrous food are required, which is equivalent to 42 oz. of ordinary solid food. By observations on the consumption of food, it is found that this is none too much, and in practice more is generally allowed. According to Prof. Parkes and Dr. Playfair the male adult requires daily about 30 oz. water-free food in active work.

The nutritive value of the army ration is estimated as follows,

| | |
|---|---|
| Nitrogenous matter, | 4.99 |
| Fats, | 4.09 |
| Carbo-Hydrates, | 15.36 |
| Salts, | 1.23 |
| | 25.67 oz. avoir. |

Dr. Smart, U. S. Army, thinks that the peace ration should be 30 oz. of properly constituted water-free food, and the field ration 35 oz.

The Navy ration contains, (Dr. Turner, U. S. N.),

| | |
|---|---|
| Nitrogenous matter, | 5.22 |
| Fats, | 4.83 |
| Carbo-Hydrates, | 17.10 |
| Salts, | 1.46 |
| | 28.61 oz. avoir. |

Malnutrition is liable to result in the disease, well known to troops, called scurvy. The preventives or antidotes of scurvy, called *anti scorbutics*, are salts of the vegetable acids. The best are potassium salts of citric, tartaric, acetic, lactic and malic acids. The acids themselves are also useful. These substances are best supplied in the form of fresh, succulent vegetables and fruits, such as the potato, cabbage, orange, lime and grape. Enforced personal cleanliness, and a supply of fresh, and especially raw meat, are useful adjuncts.

**Preparation of Food** — Cooking renders food more pleasing to the eye, agreeable to the palate, and digestible to the stomach. It develops flavor and may kill parasites and germs. It loosens and alters the texture, coagulates albumen, solidifies fibrine, and gelatinizes tendinous, fibrous and connective tissues.

The effect of cooking upon vegetables is to soften their consistence, loosen their intercellular structure, and cause the starch granules to burst, thus facilitating the penetration of the gastric juice; it coagulates albumen, and extracts gummy, saccharine and saline matter.



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The principal modes of cooking are boiling, roasting, broiling, baking, frying, and stewing.

*Boiling.* — This consists in heating the food in water. If the object be to extract the goodness of meat into the surrounding liquid, as in making soups, broths, etc., the meat is cut up finely and placed in *cold* water. After soaking for a short time, heat is applied and the temperature gradually raised. In this manner all the nutritive principles and the flavor of the meat pass into the liquid.

If the object be to retain the flavor and nutritive properties in the meat, the piece of meat should be large, it should be plunged suddenly into *boiling* water, and the boiling maintained for about five minutes. This coagulates the albumen upon the surface, leading to the formation of a more or less impermeable external layer, which precludes the escape of the juices from the substance of the meat. After this a temperature of 160° to 170° F. is maintained until the cooking is completed.

*Roasting.* — This consists in heating the food in an oven. Since the object is to retain the nutritive properties in the meat, it is first subjected to a sharp heat, and is then removed to a part of the oven lower in temperature, to allow the gradual penetration of the heat to the centre. Roasted meat is more savory than boiled, but the latter is more suited to a delicate stomach.

*Broiling.* — This is generally conducted by heating the food upon a gridiron directly over the coals. It produces the same effect as roasting, but the proportion of scorched material is greater, on account of the relatively larger amount of surface exposed.

*Baking.* — This operation is carried on by heating food in a confined space. The volatile fatty acids, being prevented from escaping, permeate the cooked articles, thus rendering them richer for the stomach than any other process of cooking.

*Frying.* — The heat in this case is applied through the medium of boiling fat or oil. The food becomes penetrated with fatty matter and thus resists the action of the gastric juice, hence this is an objectionable process of cooking for persons of weak digestive power.

*Stewing.* — The articles to be cooked are just covered with water, and should be exposed to a heat sufficient only to allow of gentle simmering. This places food in a state highly favorable for digestion.

The following table of the relative digestibility of food illustrates also the influence of the mode of preparation.

| Food. | Time required for digestion. h. m. |
|---|---|
| Rice, boiled, | 1 00 |
| Beans, boiled, | 2 30 |
| Potatoes, roasted, | 2 30 |
| Potatoes, baked, | 2 33 |
| Wheaten bread, baked, | 3 30 |
| Turnips, boiled, | 3 30 |

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| Food | Time required for digestion. h. m. |
|---|---|
| Cabbage, boiled, | 4 00 |
| Pig's feet (soused), boiled, | 1 00 |
| Eggs (whipped), raw, | 1 30 |
| Turkey, boiled. | 2 25 |
| Beef, boiled, | 2 45 |
| Beef, roasted, | 3 00 |
| Cheese, raw, | 3 30 |
| Eggs, hard boiled, | 3 30 |
| Beef, fried, | 4 00 |
| Pork, roasted, | 5 15 |

**Preservation of Food.** — The object in view in the preservation of food is to check the change which spontaneously occurs when food is exposed to ordinary conditions. This change was formerly regarded as begun by oxidation of nitrogenous matter, the latter then acting as a ferment on the other organic matter. But the researches of Pasteur and others have brought to light several special ferments, in the form of living organisms, mostly microscopic. It is, therefore, generally accepted to-day that all such changes are caused by similar organisms. These changes are favored by warmth, moisture, and the access of air.

The principal means of preserving food are, therefore,

1. By the influence of cold.
2. By drying.
3. By the exclusion of air.
4. By chemical agents.

The action of cold is explained by the fact that, below the freezing point, not only is molecular change checked, but the life of the germs is rendered more or less inactive. Preservation by cold is applied principally to animal foods, viz: in the packing of game, fish etc., and the common use of the ice-chest.

The effect of drying is probably due to the fact that moisture is necessary to preserve the life of the germs, or at least is more favorable to their active life, and also because water seems to be necessary for the decomposition of albumen. This method is applied to both animal and vegetable substances, viz: -- fish, eggs, meat, hops, potatoes, beans, apples, tea, etc.

The preservation of food by exclusion of air is the method now most commonly used. Its action may be explained, by the older theory, on the supposition that the oxygen of the air is necessary to begin the change of decomposition, by the newer theory, that the germs of fermentation or similar changes, are present in the air. The process is carried out in various ways, such as by filling up the interstices with something hot, — extract of meat, fat, syrup, oil etc.; by heating the substance in the vessel, thus destroying the oxygen in the air present, as in the preparation of condensed milk; by exhausting the air from the vessel containing the food; and by driving out the air by means of steam.

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Condensed milk is prepared by adding to rich milk about one third its weight of sugar, concentrating it in vacuo until it acquires the consistence of thin honey, and then running it into the tins, which are immediately soldered.

The most common method of canning is the last mentioned, — by means of steam.

The raw food, meat or vegetables, is placed in tins, which are immediately soldered down perfectly air-tight. The tins are then placed in a bath of boiling salt and water, and kept there about two hours and a half. At the expiration of this time they are removed and the expanded air and vapour let out through a minute aperature in the cover, by unsoldering it for a moment. After being made air-tight again they are returned to the bath, and kept there for the same time as at first, and the aperture is again unsoldered for a moment. This is again repeated. The tins are then painted and placed in the testing-room, where the temperature is sufficiently high to promote decomposition. If they show no signs of bulging out from the generation of putrefactive gases, they are considered sound.

Chemical agents act by destroying fungi and infusoria, and forming undecomposable compounds. Many are in common use. Salt extracts water, thus preventing the decomposition of albumen, and forms a liquid unfavorable to germ life. The principal chemical agents used are salt, nitre, ammonium acetate, potassium or sodium sulphite, alcohol, vineger and creosote. Smoked meat owes its preservation to the creosote formed.

### *The Ration.*

The ration for the United States Army is composed as follows: —

12 oz. pork or bacon, or 1 lb. 4 oz. fresh beef, or 24 oz. salt beef;
18 oz. soft bread or flour, or 16 oz. hard bread, or 1 lb. 4 oz. corn meal;
$\frac{15}{100}$ lb. beans or peas, or $\frac{10}{100}$ lb. rice or hominy;
$\frac{10}{100}$ lb. green coffee, or $\frac{8}{100}$ lb. roasted coffee, or $\frac{2}{100}$ lb. tea;
$\frac{15}{100}$ lb sugar; $\frac{4}{100}$ qt. vinegar; $\frac{1.5}{100}$ lb. candles;
$\frac{4}{100}$ lb. soap; $\frac{4}{100}$ lb. salt; $\frac{4}{100}$ lb. pepper.

**Meat.** — Meat is the type of the nitrogenous foods. It is of the same composition, and in the same condition, as the material it is intended to replace, hence it requires little change to be assimilated. The meat portion of the ration is large, because it has been found that animal food has certain advantages over vegetable food. It increases the amount of fibrine in the blood, raises the amount of phosphates and other salts, and renders the blood richer in red corpuscles. It tends to produce firmness of muscle, with an absence of superfluous fat, and increases the absorption of oxygen by the lungs. Animal food appeases hunger more thoroughly than vegetable, satisfies longer, and exerts a greater stimulating effect on the system. Liebig says it is essentially their food which makes carnivorous animals in general bolder and more combative than the herbivora which are their prey.

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*Composition.*

| | Fat Beef. | Fat Pork. | Dried Bacon. |
|---|---|---|---|
| Nitrogenous matter, | 14.8 | 9.8 | 8.8 |
| Fat, | 29.8 | 48.9 | 73.3 |
| Saline matter, | 4.4 | 2.3 | 2.9 |
| Water, | 51.0 | 39.0 | 15.0 |
| | 100.0 | 100.0 | 100.0 |

Less pork is issued than beef, because the former contains less water and bone, hence its nutritive value is higher; it is also used in cooking, thus utilizing material which would otherwise be wasted.

Salting diminishes the nutritive value of food by extracting nutrients. This is partially counterbalanced by the diminution in weight due to the water extracted. The diminution in nutritive power is greater in the case of beef than in that of pork, hence the same weights of salt and fresh pork are issued, but more salt beef than fresh beef. Salted and dried meat cannot be used continuously for a lengthened period without impairing the health, resulting in the disease called scurvy.

Meat cannot be subjected to adulteration, but it may be in an unwholesome state, and thereby unfit for food. Good meat has the following characters: —

It is neither a pale pink nor a deep purple tint, but intermediate in color.

The ramifications of veins of fat among the muscles produce a marbled appearance.

It should be firm and elastic to the touch and should scarcely moisten the fingers.

It should have no disagreeable odor.

It should not shrink or waste much in cooking.

It should not become wet by standing a day or so.

When dried at 100° C it should not lose over 70 to 74 per cent. in weight.

There should be no sign of the presence of parasites, when examined under the microscope. The appearance of *trichina spiralis* in pork is shown in *Fig.* 7, *Pl. VII.*

**Flour and Bread.** — Flour constitutes the most useful article of vegetable food at our disposal. It is highly nutritive and easily digestible in the form of bread, etc. It is a mixture of nitrogenous and non-nitrogenous food, in the proportion of one of the former to five of the latter. Wheat flour is preferred for making bread on account of the tenacity of its gluten. Corn meal contains more fatty matter and has a higher alimentary value.

Bread is made by converting flour into dough by kneading it with water, then baking in an oven. This furnishes *hard* bread. *Soft* bread is prepared by rendering the bread porous by filling it with interstices by means of carbon dioxide, previous to baking. One hundred lbs. of flour yield about 136 lbs. soft bread or 85 lbs. hard bread. Lime water, substituted for a portion of the water used in making the dough, improves the product from an inferior quality of flour. Good bread depends as much on the thorough incorporation of the materials as on their quality.



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Bread is rendered light and porous in order to favor digestion. This is usually accomplished by means of ferments, the principal of which are yeast and leaven. The ferments act upon the little sugar (glucose) contained in the meal, converting it into alcohol and carbon dioxide, and these gases force the tough dough into bubbles before escaping. The gluten also acts upon the starch, converting a part into maltose and then into glucose, which is transformed as before.

$$\underset{\text{Dextrine.}}{C_{18}\ H_{30}\ O_{15}} + H_2\ O = \underset{\text{Dextrine.}}{C_6\ H_{10}\ O_5} + \underset{\text{Maltose.}}{C_{12}\ H_{22}\ O_{11}}.$$

$$C_{12}\ H_{22}\ O_{11} + H_2\ O = 2\ \underset{\text{Glucose.}}{C_6\ H_{12}\ O_6}.$$

$$C_6\ H_{12}\ O_6 = 2\ C_2\ H_6\ O + 2\ CO_2.$$

*Composition.*

| | Flour. | Bread. | Corn Meal. |
|---|---|---|---|
| Nitrogenous matter, | 10.8 | 8.1 | 11.1 |
| Carbo-Hydrates, | 70.5 | 51.0 | 65.1 |
| Fatty matter, | 2.0 | 1.6 | 8.1 |
| Mineral matter, | 1.7 | 2.3 | 1.7 |
| Water, | 15.0 | 37.0 | 14.0 |
| | 100.0 | 100.0 | 100.0 |

These substances are examined to determine the percentage of water, ash and gluten. Aside from the economical considerations which condemn bread with an excess of water, there are also sanitary reasons, since bread which is too moist is prone to grow mouldy. The percentage of ash indicates the amount of mineral adulteration. The gluten is a measure of the nutritive value of the food.

*Water.* — The sample of bread, about 50 grammes, is deprived of the crust and crumbled. About 5 grammes are spread out in a thin layer in a platinum dish weighing 50 to 100 grammes; the dish is placed in a water-oven and maintained at 212° F. for 2 hours, wiped, cooled, and weighed. In case of flour or corn meal one gramme is used, and heated only to 200° F.

*Ash.* — Ten grammes of flour or bread are burnt in a platinum crucible, the weight of the residue determines the ash. Care must be taken not to mistake the hard cake first formed for the ash. In case the ash is over 0.8 per cent., in case of flour, or over 2.0 per cent., in case of bread, it is examined for mineral adulteration.

**Alum** is sometimes added to arrest the change in the gluten and restore incipient, unsoundness of flour. The objection to its use is its effect on digestion, producing constipation, etc. Alumed bread is rare, nevertheless, in time of war or famine, the fraud may be more frequently practiced. For its detection 50 grammes flour or 100 grammes bread are placed in a weighed platinum dish, capacity 200 c. c., and ignited over a large Bunsen burner for several hours, at a moderate temperature, but with a large supply of air. The ignition is continued until the flour-ash does not exceed one gramme, the bread-ash two grammes, in weight. The ash is

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moistened with 3 c. c. pure strong hydrochloric acid (sp. gr. 1.2), and then 30 c. c. distilled water are added, the whole boiled, filtered, and the residue washed with boiling water. The residue is ignited and weighed, it consists of sand and silica. The filtrate is mixed with 5 c. c. of ammonia (sp. gr. 0.88), and afterwards with 20 c. c. of moderately strong acetic acid, taking care that at least 10 c. c. are added after the establishment of an acid reaction. The liquid is boiled and filtered. The precipitate, consisting of aluminium and iron phosphates, is well washed with boiling water, ignited and weighed.

It is then dissolved in acid and diluted to 100 c. c. The iron in this solution is determined by titration with potassium ferro-cyanide. A standard iron solution is prepared by dissolving one gramme fine iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing the ferric oxide obtained, dissolving it in a little hydrochloric acid and diluting accurately to one litre. One c. c. contains one milligramme iron as ferric chloride. This is diluted 100 times for use. Ten c. c. of the solution to be tested are placed in a Nessler glass, one c. c. concentrated hydrochloric is added, then 1 c. c. potassium ferro-cyanide and the solution shaken. The depth of color is imitated by means of the standard iron solution and the ferro-cyanide solution, adding as before one c. c. hydrochloric acid.

One part iron furnishes $\frac{151}{56}$ parts iron phosphate, $Fe\,PO_4$, hence, multiplying the amount of iron obtained above by $\frac{151}{56}$ gives the weight of iron phosphate. Subtracting this from the total weight of the precipitate determines the weight of aluminium phosphate. Since 100 grammes unalumed flour or bread contain 0.008 gramme aluminium phosphate, this must be deducted. To calculate the aluminium phosphate, $Al\,PO_4$, into alum, $Al\,NH_4\,S_2\,O_8 . 12\,H_2\,O$, we have the proportion, from their molecular weights,

$$122.4 : 453.4 :: 1 : x = 3.7.$$

Multiplying the weight of phosphate by 3.7 gives the weight of ammonia alum in 100 grammes bread or 50 grammes flour.

Cupric sulphate is sometimes used for the same purpose as alum. To detect it, 100 grammes flour or bread are incinerated in a platinum dish, the ash moistened with a few drops of sulphuric acid, warmed and allowed to cool. A little water is added, and a little piece of clean zinc or iron placed in it. Copper, if present, will be deposited, and may be recognized by its red color. The spot of copper may also be dissolved in a drop or two of boiling sulphuric acid, and ammonia added in excess, producing the usual purple color. Finally, the ammonia may be driven off by heat, and potassium ferro-cyanide added, producing a brown precipitate, which last is one of the most delicate tests known.

*Gluten.* — Gluten is a mixture of vegetable fibrine and vegetable gelatin ; it is a grayish, adhesive, elastic, insoluble substance. One of the best — if not the very best — criterion of the genuineness of a flour is that it should yield a proper amount

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of gluten. The quality of the gluten is best determined by converting the flour into dough. The gluten is determined by weighing 10 grammes of flour, and placing it in a heap in the centre of a glazed, white porcelain tile 7 inches square. Four c. c. distilled water are dropped on the flour, and the mixture is worked together with a palette knife, until all the flour has been incorporated to form a stiff paste.

The ball of dough is then placed in a stout cylindrical glass, capacity 200 c. c., about 50 c. c. of water poured in, and by means of the palette knife the ball of dough is worked up with the water, the starch granules becoming separated, leaving a mass of gluten. The water containing the starch is carefully decanted off, fresh water added, and the washing repeated, until all the starch is removed. The gluten is then placed in ether, and worked by means of a glass rod, to remove a little fatty matter and to partially dry the gluten. By means of the glass rod it is transferred to a platinum dish and spread out in a thin layer. The dish is heated in a water oven until it ceases to lose weight. The weight of gluten found must be corrected, 0.3 per cent. of the flour, for ash, one per cent. for fat, hence, the percentage of gluten is determined by subtracting 1.3, after multiplying the gluten found by 10. Flour containing less than 8 per cent. gluten should be rejected.

*Total Nitrogenous Matter.* — To determine the total nitrogenous matter in flour, or any other vegetable substance, one gramme is placed in a litre flask, and 20 c. c. of potassium hydrate solution (5 grammes KHO to 100 c. c. water) are added, then water to the litre mark, and the contents of the flask shaken up. One c. c. contains one milligramme flour, etc.

A retort is arranged as in water analysis, 300 c. c. of good drinking water placed in it, 50 c. c. of the potassium permanganate and caustic potash solution added, and the liquid distilled until no more ammonia is evolved. Twenty c. c. of the liquid containing the vegetable substance are added, the liquid is distilled and Nesslerized. Wheaten flour yields between 1.00 and 1.13 per cent. of its weight of ammonia. Unsoundness is indicated by a lower yield.

*Cold Aqueous Extract.* — The starch, gluten, fat and part of the ash of flour are insoluble; the modified starch, the vegetable albumin and another part of the ash are soluble. In proportion as the flour is unsound, the starch is altered, hence the aqueous extract will be large in the same proportion.

To determine the cold aqueous extract 100 grammes flour are stirred up with distilled water in a large porcelain basin, the mixture poured into a litre measure, diluted to the mark, the contents then poured into a beaker, from this on a large filter and filtered. The first small quantity of filtrate is rejected; 50 c. c. of the filtrate are collected and accurately measured, evaporated to dryness in a platinum dish in a water oven, and weighed. Multiplying by 20 gives the quantity of extract furnished by 100 gramme flour, or the per centage. Sound flour yields 5 per cent. of its weight of cold aqueous extract, dried at 100° C.

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The maltose in the cold aqueous extract (about 1.2 gramme), may be measured by Fehling's solution, 10 c. c. of which equal .0779 gramme maltose.

*Composition.*

| | Best Wheaten Flour. | Good Bread. |
|---|---|---|
| Water, | 16.5 | 34.0 |
| Ash, | 0.7 | 2.0 |
| Fat, | 1.5 | |
| Gluten, | 12.0 | 9.5 |
| Vegetable Albumen, | 1.0 | |
| Modified Starch, | 3.5 | |
| Starch Granules, | 64.8 | 54.5 |
| | 100.0 | 100.0 |

*Alterations and Adulterations.* — In moist situations flour is injured, its gluten losing its tenacity and becoming more or less soluble; its original qualities may be restored partially, by substituting for part of the water used in making the dough, 27 lbs. of lime water for every 100 lbs. flour.

Flour is little adulterated at present. The principal adulterations on record are by the flour of other grains, such as barley, bean, pea, potato, rice, etc. The character of the envelope is essentially different in the different grains, and the character of the starch granules also varies. These adulterations can only be detected by the microscope. Mineral adulterations, such as alum, clay, gypsum etc., are detected by chemical means.

Flour which has become damp is liable to disease and the consequent development of fungi and mites, such as the acarus farinæ and the weevil.

**Beans and Peas.** — These are the typical vegetable nitrogenous foods, containing three parts nitrogenous to five parts non-nitrogenous organic matter.

*Composition.*

| | Beans (dried). | Peas (dried). |
|---|---|---|
| Water, | 8.40 | 8.3 |
| Nitrogenous matter, | 29.05 | 23.8 |
| Starch, | 55.85 | 58.7 |
| Cellulose, | 1.05 | 3.5 |
| Fat, | 2.00 | 2.1 |
| Salts, | 3.65 | 2.1 |
| | 100.00 | 98.5 |

Beans or peas and rice or hominy are issued under opposite circumstances. When the meat portion is deficient beans or peas are issued, when the meat portion is in excess rice or hominy are issued.

Beans and peas are used in the young and fresh state, and also dried and preserved while still green, so as to be available all the year round. In this latter condition they require to be soaked in water for some hours before being cooked. They are

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grown and eaten in all parts of the world, and are everywhere regarded as very nutritious when they can be digested. Nothing, however, but the most prolonged cooking will serve to help in this particular. If old, the longer they are boiled the harder they become. On account of the small quantity of carbonaceous matter present they are invariably associated with fat, when eaten.

Peas when putrid, undergo some peculiar change not yet investigated, resulting in the formation of a poison. Peas preserved in tins are sometimes previously boiled in a copper vessel, which imparts a fine green color, the chlorophyll having been rendered insoluble by the copper. It may be detected by making a paste of a weighed quantity of peas with water and a little hydrochloric acid, in a platinum dish, and inserting a rod of zinc in contact with the platinum. The galvanic current produced causes the copper to be deposited as a thin film, which may be dried and weighed.

**Rice and Hominy.** — These are the typical vegetable non-nitrogenous foods, containing thirteen parts non-nitrogenous to one part nitrogenous matter.

Rice is said to supply the principal food of nearly one-third of the human race. It is characterized by the large proportion of starch, and the small proportion of nitrogenous matter it contains. It must therefore be associated with other articles to compensate for the deficiency of the latter. It is easily digestible, and is best cooked by thoroughly steaming.

*Composition.*

| | |
|---|---|
| Nitrogenous matter, | 6.3 |
| Carbo-Hydrates, | 79.5 |
| Fatty matter, | 0.7 |
| Saline matter, | 0.5 |
| Water, | 13.0 |
| | 100.0 |

Hominy is made from ripe corn, the grains being deprived of their hull, and broken or coarsely ground. It is characterized by the large amount of fatty matter it contains. It also contains a large amount of nitrogenous matter and therefore has a high alimentary value. It is the cheapest food we have. Its composition is similar to that of corn meal already given.

These substances are so cheap that they are rarely, if ever, adulterated. The presence of other starches would be readily detected under the microscope.

**Coffee and Tea.** — These constitute useful beverages. They produce an invigorating and restorative effect on the system, which is not followed by any depression. They arouse the mental faculties and the energies generally. They increase the activity of the skin and retard the transformation of tissue. They possess the power of relieving hunger and fatigue, and are equally serviceable against heat and cold. As ordinarily consumed, with milk and sugar, they furnish direct nourishment in no inconsiderable amount.

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*Composition.*

| Raw Coffee. | | Green Tea. | |
|---|---|---|---|
| Cellulose, | 34.00 | Cellulose, etc., | 31.66 |
| Water, | 12.00 | Water, | 9.37 |
| Fat, | 13.00 | Tannin, | 18.69 |
| Glucose, etc., | 15.50 | Gum, | 5.89 |
| Legumin, | 10.00 | Albuminous matter, | 24.39 |
| Potassio-caffeine caffeate, | 5.00 | Theine, | 2.79 |
| Nitrogenous matter; | 3.00 | Chlorophylle, etc., | 1.83 |
| Caffeine, free, | 0.80 | Ash, | 5.38 |
| Essential Oil, | 0.03 | | 100.00 |
| Ash, | 4.00 | | |
| | 97.33 | | |

Coffee beans are the seed of Caffea Arabica, a tree which grows in the West Indies, Arabia, Brazil, Java, Ceylon and other warm countries. The seeds are separated from their soft pods, washed and dried, and lastly freed from their parchment-like coating and sent into market. It is met with in three conditions, — raw, roasted, and ground.

Roasting coffee develops the aroma, the coffee beans increase in volume but diminish in weight, the sugar is converted into caramel and the coffee is rendered more soluble in boiling water. Exposed to the air roasted and ground coffee loses its aroma in two or three months, but if packed in tins it will keep for a longer period.

In preparing coffee it must not be boiled or the aroma is partly dissipated.

Ground coffee is most liable to adulteration, the principal of which is chicory, which is largely cultivated for this purpose. The roots of the chicory are dried, roasted, and ground and then mixed with the coffee. Other adulterations are roasted corn and beans, potato starch and sugar.

These adulterations are best detected under the microscope. Adulteration of coffee with chicory is represented in *Fig.* 9, *Pl. VII.* When dropped in cold water, coffee floats for some time, while chicory sinks; coffee gives no sensible color, chicory rapidly produces a yellowish-brown solution. As coffee contains no starch this may be detected by the blue color produced with iodine.

Tea is the *prepared* leaves of Thea sinensis, a shrub, usually five feet high, growing in China, Japan and the Himalaya. The varieties are derived from the same plant and differ only in age and mode of preparation. Black tea differs from green in having undergone a kind of fermentation, which has altered the color.

The adulterations of tea are of three kinds, — it may be sanded, mixed with leaves which are not tea, or it may be spent tea.

The microscopic appearance of the tea leaf is represented in *Fig.* 8, *Pl. VII.*

**Sugar.** — Cane sugar, $C_{12}$ $H_{22}$ $O_{11}$, occurs abundantly in vegetables, and forms an important alimentary principle. Being soluble it is easily digested, but is sometimes

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apt to undergo the acid fermentation. It is the type of sweet substances, hence its use in sweetening and flavoring.

Sugar is probably the purest food substance in commerce. loaf sugar, is, as a rule, chemically pure. The finest purified sugars are white, crystalline and not moist to the touch. Raw sugars are sometimes adulterated with starch, sand, glucose and water.

*Insoluble Impurities.* — These are determined by dissolving five grammes in cold water and examining the residue under the microscope. The best sugars leave merely a few minute fragment of cane floating in the water. Starch is detected by the blue coloration produced by addition of a drop of iodine solution to the residue.

*Moisture.* — Two or three grammes of sugar are weighed on two tared watch-glasses, about 66 mm. in diameter, placed in a drying oven, and dried for three hours at 110° C. After drying the lower watch glass is clamped over the one containing the sugar, and the whole is re-weighed as quickly as possible. The loss of weight determines the moisture.

*Ash.* — The dried sugar is incinerated in a small platinum dish at a red heat, the weight of the dish and residue after ignition, less the weight of the dish when empty, determines the ash.

*Glucose.* — Glucose, $C_6 H_{12} O_6$, is the most common adulteration of raw sugar and its derivatives. It is now extensively manufactured from starch, and largely used to adulterate syrup. The main objection to it is its low sweetening power, being to that of cane sugar in the proportion of 2 : 5.

An adulteration of cane sugar with glucose is easily detected. The principle involved in the process is that glucose readily reduces cupric salts in presence of alkalies.

$$Cu\,SO_4 + 2\,KHO = K_2\,SO_4 + Cu\,H_2\,O_2.$$
$$15\,Cu\,H_2\,O_2 + C_6\,H_{12}\,O_6 = 6\,Cu_2\,O + 3\,(CHO_2)_2\,Cu + 18\,H_2\,O.$$

Two solutions are prepared.

No. 1, consisting of 34.639 grammes cupric sulphate (c. p.), crystallized, dissolved in 500 c. c. distilled water.

No. 2, consisting of 173 grammes potassio-sodic tartrate in 400 c. c. distilled water, mixed with 100 c. c. soda-lye, containing 400 grammes to the litre. These solutions are kept separately, in blue glass bottles, and mixed in equal volume when a test is to be made. Ten c. c. equal .05 gramme glucose.

To make an estimation a preliminary test is made to determine the approximate strength of the sugar solution. Ten c. c. of the mixed solutions are measured into a porcelain dish, diluted with an equal volume of water, and boiled quickly. There should be no precipitate formed. The sugar solution, which should be of such a strength that 25 to 50 c. c. are required to reduce 10 c. c. of the copper solution, is added from a burette as rapidly as possible, without risk of running in a excess.

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The blue color gradually changes and is replaced by the red color of the cuprous oxide formed. The latter is allowed to settle. The color of the solution when all the copper is precipitated should be clear pearl white. To determine the end point with greater exactness a little of the liquid is removed in a pipette, filtered, acidified with acetic acid and a drop of potassium ferro-cyanide added, which will strike a brownish-red color so long as copper remains in solution.

The sugar solution is diluted to contain one per cent. of glucose. Fifty c. c. of this are heated to boiling for 2 to 4 minutes, with a quantity of undiluted copper solution, judged to be nearly that necessary for reduction. The liquid mixture is then thrown on a filter and the filtrate tested for copper with acetic acid and potassium ferro-cyanide. If the metal is present a new experiment is made with the same quantity of sugar solution and less copper solution, and so on, until in two consecutive experiments, differing by $\frac{2}{10}$ c. c. copper solution, the filtrate of one shows copper while that of the other does not.

*Analyses.*

| | West India, Raw. | Beet, Raw. | Good Centrifugal. | Fair Centrifugal. | Refined. |
|---|---|---|---|---|---|
| Cane Sugar. | 94.4 | 95.4 | 96.50 | 92.50 | 99.899 |
| Glucose. | 2.2 | 0.3 | 0.80 | 2.10 | none. |
| Organic matter | 0.3 | 0.4 | 0.60 | 1.65 | none. |
| Ash. | 0.2 | 1.6 | 0.35 | 0.55 | 0.023 |
| Water. | 2.8 | 2.0 | 1.75 | 3.20 | 0.078 |

**Condiments.** — These are rather adjuncts to food than foods proper, but they are of extreme value in rendering food more palatable, stimulating the appetite, supplying a necessary substance and assisting in the preservation of food.

*Salt.* — Salt, Na Cl, is essential to man and the lower animals. It renders food more palatable, stimulates the sense of taste and increase the flow of saliva. It furnishes hydrochloric acid, an essential constituent of the gastric juice, and sodium chloride, carbonate, etc., essential to the insolubility of the blood corpuscles. Vinegar favors the liberation of hydrochloric acid from salt, forming with the sodium at first a neutral salt, sodium acetate, and then an alkaline salt, sodium carbonate, both of which seem to be important in the animal economy. The constant quantity of salt in the blood is an indication of its necessity; it is probably an agent of diffusion, converting colloidal substances (albumen, etc.), into crystalloids, thus aiding absorption and secretion.

*Pepper.* — Pepper and spices have been in use in all ages and were always highly esteemed. The black and white pepper of commerce are prepared, by grinding, from the berry of Piper Nigrum, a shrubby, climbing plant, growing in the East Indies. In the latter the dark brown cuticle has been removed before grinding.



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Pepper is adulterated with a multitude of substances, principally pepper dust, faded leaves, linseed meal, husks of mustard, ground rice, sand, flour, woody fibre, salt, etc., all of which are readily detected under the microscope.

*Vinegar.* — Vinegar is an acid liquid produced by the acetous fermentation of saccharine substances or the oxidation of alcohol.

$$C_{12} H_{22} O_{11} + H_2 O = 2 C_6 H_{12} O_6.$$
$$C_6 H_{12} O_6 = 2 C_2 H_6 O + 2 CO_2.$$
$$C_2 H_6 O + 2 O = C_2 H_4 O_2 + H_2 O.$$

Commercial vinegar is a more or less impure acetic acid, $C_2 H_4 O_2$. Its use is to flavor food and stimulate the sense of taste; it is also converted into carbonic acid and so far acts as a direct food.

During the acidification the nitrogenous matter assumes the form of *mother of vinegar*, a living organism, *Mycorderma Aceti*, capable in itself of producing the acetous fermentation.

Vinegar must be kept in close casks as it is liable to undergo a putrefactive decomposition. This change is favored by a slight motion, hence, vinegar does not keep well in cellars exposed to vibrations such as are occasioned by the rattling of carriages.

The principal impurities and adulterations of vinegar are water, mineral acids, generally sulphuric, metallic impurities (arsenic, copper, lead, zinc and tin), and organic coloring matters.

Water renders the vinegar weak in its essential constituent. Its specific gravity should be 1.022, and it should contain five per cent. of acetic acid. The acidity is determined by adding an excess of carefully weighed pure calcium carbonate to a known weight of the vinegar; the liquid is boiled, filtered, the residual calcium carbonate dissolved in slight excess of standard hydrochloric acid solution and titrated back with sodium hydrate, using litmus, or better, cochineal, as an indicator. From the amount of carbonate thus found to have been unacted on by the vinegar, the total acidity is calculated.

Hydrochloric acid is readily detected by the white, curdy precipitate produced with silver nitrate. Sulphuric acid cannot be detected by barium chloride, as this test fails to distinguish between free sulphuric acid and soluble sulphates. The total free mineral acid is determined by mixing 50 c. c of the vinegar with 25 c. c. of decinormal sodium carbonate solution; the liquid is evaporated on a water bath in a platinum dish, the residue dried at 110° C and carefully incinerated at the lowest possible temperature — the ash need not be burned white. Twenty-five c. c. of a decinormal solution of sulphuric acid are now added to the ash, the liquid heated to expel free carbon dioxide and filtered. The filter is washed with hot water, litmus or cochineal added, and the acidity determined by decinormal sodium

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carbonate solution. The volume necessary for neutralization directly gives the proportion of free mineral acid, 100 c. c. being equal to 0.49 gramme $H_2 SO_4$.

Metallic impurities are determined by saturating the liquid with sulphydric acid. A black precipitate indicates iron, copper or lead. After supersaturation with ammonia and subsequent addition of sulphydric atid, zinc is indicated by a white precipitate. Arsenic is detected by Marsh's test.

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# METRIC SYSTEM.

*Measures of Length.*

| Metre. | | Decimetre. | | Centimetre. | | Millimetre. |
|---|---|---|---|---|---|---|
| 1 | = | 10 | = | 100 | = | 1000 |
| | | 1 | = | 10 | = | 100 |
| | | | | 1 | = | 10 |

1 Centimetre = 0.3937079 Inch.

1 Inch = 2.5399541 Centimetre.

*Measures of Surface.*

1 Square Inch = 6.4513669 Square Centimetres.

1 Square Centimetre = 0.1550059 Square Inch.

*Measures of Capacity.*

| Litre | | Decilitre or 100 Cubic Centimetres. | | Centilitre or 10 Cubic Centimetres. | | Millilitre or Cubic Centimetre. |
|---|---|---|---|---|---|---|
| 1 | = | 10 | = | 100 | = | 1000 |
| | | 1 | = | 10 | = | 100 |
| | | | | 1 | = | 10 |

1 Cubic Inch = 16.387534 Cubic Centimetres.

1 Cubic Centimetre = 0.061022 Cubic Inch.

1 Fluid Ounce = 29.568 Cubic Centimetres.

1 Cubic Centimetre = 0.03331 Fluid Ounce.

*Measures of Weight.*

| Gramme. | | Decigramme. | | Centigramme. | | Milligramme. |
|---|---|---|---|---|---|---|
| 1 | = | 10 | = | 100 | = | 1000 |
| | | 1 | = | 10 | = | 100 |
| | | | | 1 | = | 10 |

1 Gramme = 15.432349 Grains.

1 Grain = 0.064799 Gramme.

*Measures of Work.*

1 Kilogrammetre = 7.23352 Foot Pounds.

1 Foot Pound = 0.13825 Kilogrammetres.

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Fig. 1.

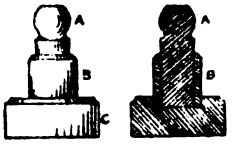


Fig. 2.

Fig. 3.

Fig. 6.

Fig. 5.

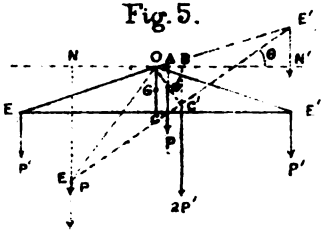

Fig. 4.

Fig. 8.

Fig. 7.

Fig. 10.

Fig. 11.

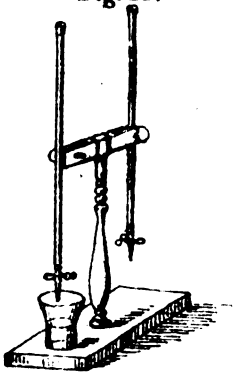

Fig. 12

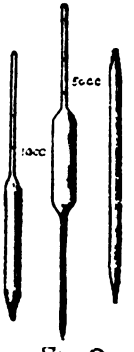


Fig. 9.

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PLATE II.

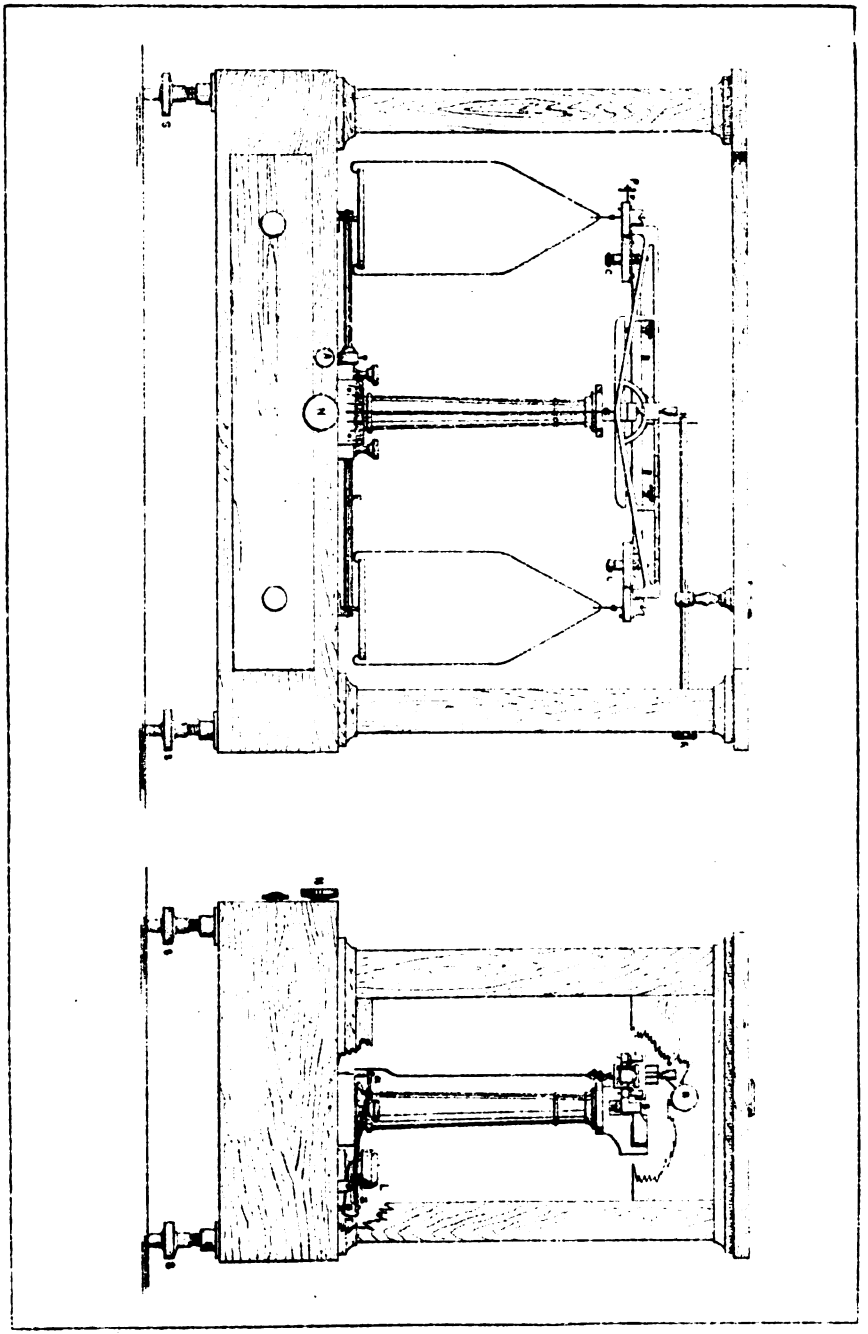

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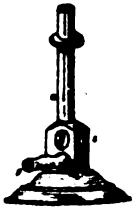
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.



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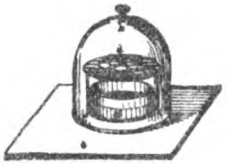
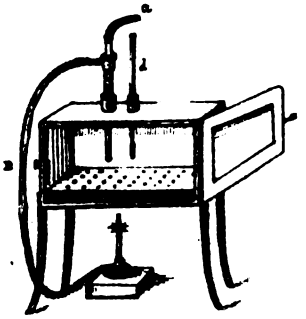


Fig. 6.

Fig. 7.



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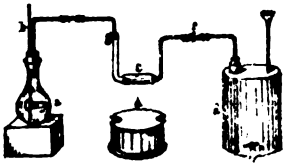

Fig. 8.

Fig. 11.

Fig. 10.

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Fig. 1.

Fig. 2.

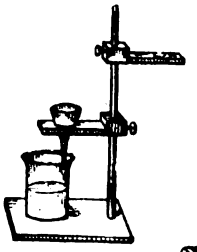
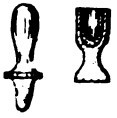


Fig. 3.

Fig. 6.

Fig. 4.

Fig. 7.



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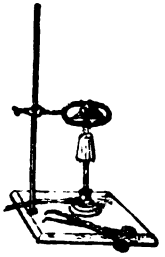

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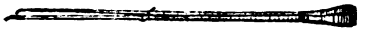

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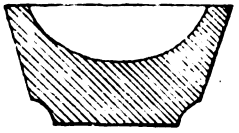

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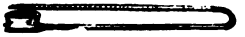

Fig. 11.

Fig. 14.

Fig. 15.

Fig. 12.

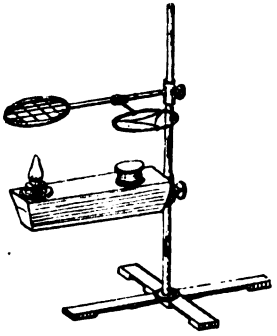

Fig. 16.

Fig. 17.

Fig. 18.

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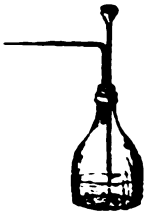

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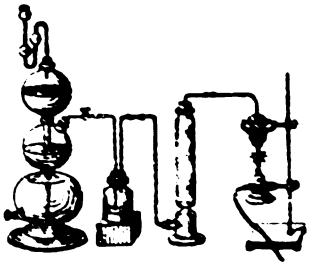

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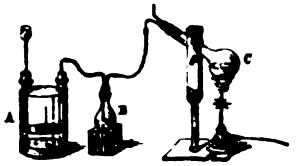


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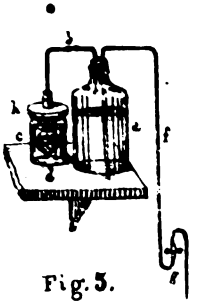


Fig. 5.

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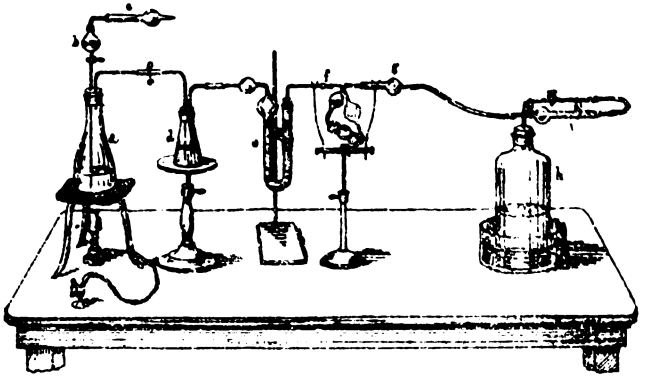


Fig. 6.

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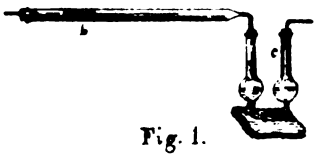

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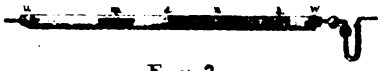

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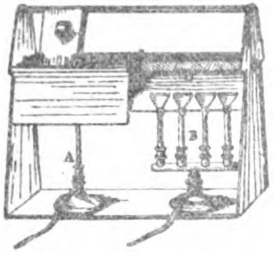

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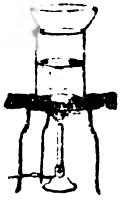

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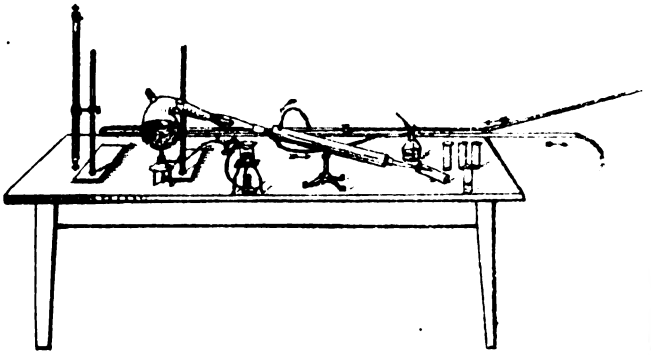

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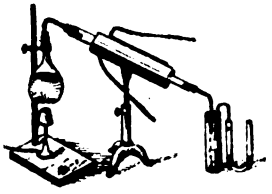

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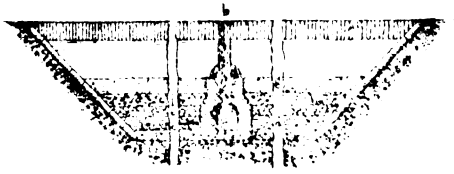

Fig. 9.

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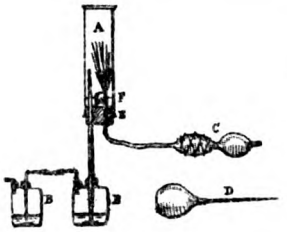


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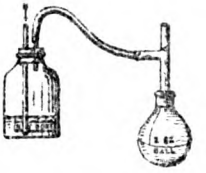

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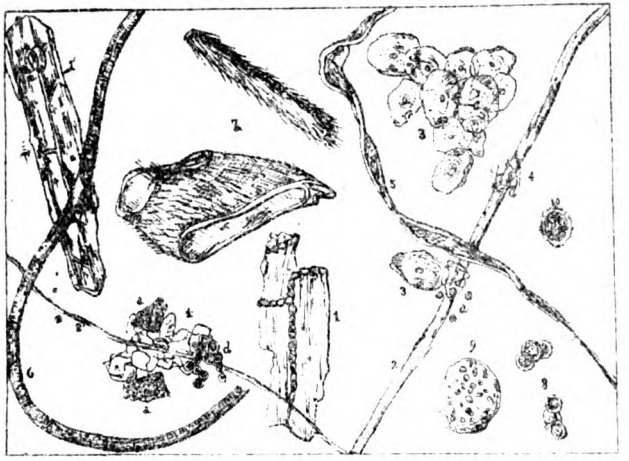

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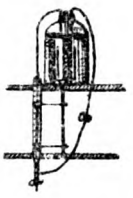

Fig. 6.

Fig. 9.

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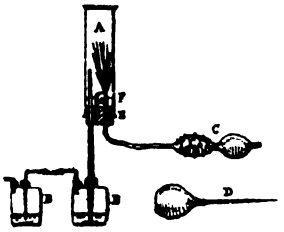


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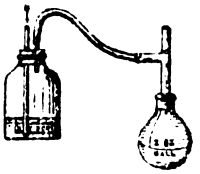

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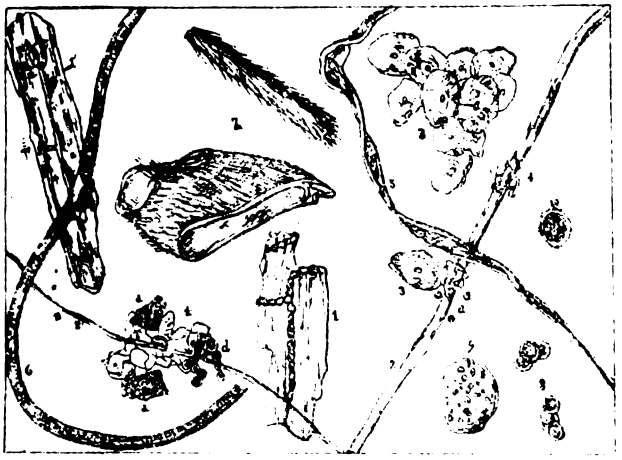

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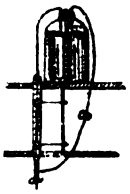

Fig. 6.

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